

MECHANISM OF SHORT-TERM CLAY-LIME
STABILIZATION

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by

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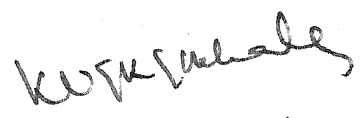
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CERTIFICATE

Certified that the work presented in this thesis has been carried out by Sri Gautam Chaudhuri under our supervision and has not been submitted elsewhere for a degree.


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ABSTRACT

✓ The mechanism of clay - lime stabilization during shorter periods has been undertaken for study together with an attempt at understanding of the dependence of the Atterberg limits and strength parameters on the same. ✓ The present investigation reveals the following sequence of events during the process:-)

An initial adsorption of Ca-ions ^{takes place} into the lattice and onto the surface of the clay to various amounts depending on the nature of the clay; In bentonite such adsorption is upto 4 percent while in kaolinite it is restricted to 2 percent. Simultaneously with adsorption in these clay minerals also proceeds certain reactions resulting in the formation of prehnite (a calcium aluminate silicate) ^{that} is evidenced even in the first 24 hours of aging which increases with time. Subsequent formation of hydrogarnets, tetra calcium aluminates and calcium aluminate silicates has also been noticed from X-ray diffraction studies. In bentonite while in the intial stages calcium aluminate silicate and crystallized calcium silicate hydrate have developed, subsequent growth of ill-crystallised tobermorite and tetra calcium aluminate took place. The rate of changes in the quantities of montmorillonite, kaolinite

and free silica as also rate of growth of new minerals have been attempted for intensity computations of selected peaks for these constituents at different stages of the reactions.)

✓ The changes in the liquid limit, plastic limit and shrinkage limit for the kaolinite - lime and bentonite - lime systems have been correlated to the processes that are operative during such a mechanism of clay - lime stabilization and consequent changes in the hydration and dehydration patterns of the systems.

✓ The strength variations are explained on the basis of the nature and extent of new products developed, the physical changes that take place in respective systems and the excess lime that is present.

CHAPTER I

STATEMENT OF THE PROBLEM

So much work has been done on soil stabilization all over the world that it is a surprise to find that answers to some of the rather obvious fundamental questions have not been provided so far. For example, the most general question is - what are the changes at the macroscopic and microscopic level in clay that reflect its physical and mechanical behaviour during lime interaction? The role of ion exchanges had been a guess for several years but a statement on its certainty and precise nature is yet awaited.

Similarly, the question as to whether flocculation and carbonation have any dominant role in the soil-lime stabilization mechanism has yet to be answered. Though attempts have been made on these aspects, general acceptable understanding on the same has not yet been reached.

X-ray diffraction studies of the clay-lime mixtures at different lime levels and on various aging periods would enable one to precisely indicate the strain and other modifications in the clay lattice induced by the Ca(OH)_2 interaction as also the tracking of the new products like hydrous calcium aluminates and silicates. Though preliminary attempts by a few workers have been made on the formation of these new products, their rate of growth and correlation with engineering behaviour of

clay have not been provided. Progress in the last decade or two in cement technology has provided the necessary data for research into the composition and structure of such phases in the $\text{CaO-Al}_2\text{O}_3\text{-H}_2\text{O}$, $\text{CaO-SiO}_2\text{-H}_2\text{O}$ and $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3\text{-H}_2\text{O}$ systems. The present study is an attempt to determine (1) The nature of variations of physical properties involved in the clay - lime stabilization, (2) Whether these changes are the same for expanding and non expanding clays or are there any possible differences, (3) The possible lattice modifications at different lime levels in clays and their variation on aging, (4) The nature of new chemical compounds that form during clay - lime interaction and effect of aging on the same and (5) The correlation of engineering behaviour with the macroscopic and microscopic changes during the stabilization process. Within the available time it is neither realistic nor possible to undertake investigations with clays as also soils, the author has restricted his investigations to pure clay materials with the hope that the results obtained in the present study would be largely the basis for any such future investigations with soils in the field and laboratory.

CHAPTER II

STATUS OF THE EXISTING LITERATURE

To improve the engineering properties of cohesive soils, specially expansive type, the wide range of chemical reagents (both organic and inorganic) are available. Among the inorganic additives the use of hydrated lime has been growing in the field of soil stabilization because of the ease, effectiveness and economy.

Extensive investigations have been undertaken by several workers on clay - lime stabilization because of the obvious practical applications. Available literature indicates several distinct approaches in the past on the study of this subject. The important trends of thinking on the process of soil - lime stabilization include (1) Cation exchange - replacement of available cations like Na, K or Mg by Ca cations, (2) Aggradation and consequent increase in effective grain size through flocculation, (3) Carbonation that is reaction of lime with the CO_2 from the atmosphere to form CaCO_3 which induces cementation in the system and (4) Pozzolanic reactions that yield products of cementing nature.

The cation exchange properties of clay has been aptly summarized by Carroll (1959). Although many natural soils are almost calcium saturated,

they exhibit all classic deficiencies in their structure that require stabilization treatment. It has also been established that even when lime is added to a dilute clay suspension in quantity exceeding that required for complete saturation, no complete exchange by Ca ion takes place (Diamond and Kinter, 1966). However clay - lime stabilization does not involve ion exchange alone since fluctuations of ground water levels and percolating ground waters might replace the Ca ions thus reducing the beneficial effect of added lime (Eades and Grim, 1960).

When lime is added to the clay, an immediate dominant flocculation ensues. According to modern Colloidal - chemical concepts, the electrolytic double layer gets modified with consequent decrease in the electro - static repulsive forces (Van Olphen, 1963). The net attraction increase brings about the flocculation. Work in this direction has also been reported by Davidson and Handy (1959). The dependence of water retention properties in clay during stabilization has also been reported by these authors.

Formation of calcium carbonate during stabilization has been established by Eades, Nichols and Grim (1962). But neither the cementing nature of the carbonates nor their influencing nature on the strength parameter of the clay involved have been studied by them.

Diamond and Kinter (1966) believe that the long term reaction of uncarbonated lime with the soil itself would far outweigh any such contribution and that the carbonation is probably a deleterious rather than a helpful phenomenon in soil stabilization.

The cementitious products formed from reactions of lime with clay minerals have been studied by several workers (Eades and Grim, 1960; Sloane, 1964; Croft, 1964; Davidson et al 1966; and Diamond and Kinter, 1966). During such process two stages of reaction are visualised (1) immediate rapid process that modify the response of the soil system to water and (2) slow but long term reactions that cause formation of final interaction product. Among the former are included such properties as liquid limit, plastic limit, swell pressure, volume change on drying and permeability.

A general increase of plastic limit with increasing lime level takes place (Hilt and Davidson, 1960). However conflicting report exists on the effect of lime on liquid limit. Wang et al (1963), Jan and Walker (1963) report a decrease in the liquid limit while a substantial increase in liquid limit has been reported by clare and Cruchley (1957) and Zolkov (1962). Apparently this variation has been due to the sensitive nature of the clay to the cation present (Grim, 1957). That these variations continue upto

some limiting lime content designated as "lime fixation point" has been reported by several workers. Effect of aging has also been discussed by Wolfe and Allen (1964).

Drastic volume changes involved in the clay-lime stabilization have been discussed by Lund and Ramsey (1959), Wolfe and Allen (1964), Mitchell and Hooper (1961), Croft (1964) and Katti et al (1966). The variation of shrinkage and swelling were dependent on the type of clay involved. Many workers have also reported that the density to which a soil can be compacted at a given moisture content is usually reduced significantly when lime is added and delay in compaction causes a further reduction in density. Herrin and Mitchell (1961) indicated that beyond about 5 percent of lime by weight, little additional increase in the optimum moisture requirement takes place.

Strength of the clay - lime mixture is greatly influenced by the interaction during clay - lime stabilization and through the formation of the new products. The variation of strength during soil - lime stabilization has been dealt in detail by several workers (Hilt and Davidson, 1960; Eades and Grim, 1960; Mitchell and Hooper, 1961; Croft, 1964 and Katti et al, 1966). Mitchell and Hooper (1961) indicated the importance of reduction of time interval between mixing of clay lime with

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water and subsequent compaction. The strength gain in a clay mineral on application of lime is also dependent on the mineralogical composition of clays (Croft, 1964, Evstatiev et al 1967, Grim, 1967) .

Diamond (1964) has reported that lime reacts almost instantaneously with hydrous alumina of high surface area to produce the well crystallized compound tetra calcium aluminate hydrate. Such immediate reaction in the clay-lime systems has been indicated by Diamond and Kinter (1966) .

The significant aspect that perhaps influences to the maximum extent the strength parameter of clay during stabilization with lime is the long - term reaction products. Reaction of lime with clay minerals (hydrous aluminate silicates) produces compounds largely of two classes - hydrated calcium silicates and hydrated calcium aluminates. Except under the hydrothermal environment, ordinarily the hydrated calcium silicates are fully crystallized. Three such phases have been reported so far (Diamond and Kinter 1966) . There are several types of calcium aluminate hydrates but the form generally produced in clay lime reaction is C_4AH_{13} ($C=CaO$, $A=Al_2O_3$, $H=H_2O$) . A comprehensive account of these calcium silicates hydrates and calcium aluminate hydrates has been provided by Taylor (1964) . Calcium Silicate hydrate (1), $CaO-SiO_2$ ^{product} aqueous, and $3CaO-2SiO_2$ - ^{product} aqueous; have recently been prepared hydrothermally in a crystalline condition.

The calcium silicate hydrate (1) appears to be the final product of hydrothermal treatment of mixture of lime:

Silica ratio of 1: 1 at 110°C. It is obtained only as an intermediate product at higher temperature upto at least 320°C. Reactions have also been conducted and products examined at various lime silica ratio in the system $\text{CaSiO}_3 - \text{H}_2\text{O}$ (Buckner, Roy and Roy, 1960, Heller and Taylor, 1952a, 1952b). The most common calcium - Silicate - hydrate group. the tobermorite group has been examined in detail and the crystal structure analysis attempted (Taylor, 1964; Megaw and Calshey, 1956).

Goldberg and Klein (1952) have been the first to publish on the x-ray study of clay - lime reaction product. However only calcium carbonate was detected by them. Among the subsequent workers that dealt with x-ray studies in stabilization, mention can be made of Eades and Grim (1960), Hilt and Davidson (1961), Glenn and Handy (1963), Diamond, White and Dolch (1963) and Arizumi et al (1962). However most of these studies did not discuss the possibility of formation of the compounds in the quaternary lime - silica - alumina - water system.

CHAPTER III

MATERIALS AND METHODS

To understand the variation of physical properties during stabilization and the process involved, individual clay fractions have been chosen as the starting materials rather than soils. The specific intention in such a selection was that the behaviour and the processes involved during the soil-lime stabilization are rather complex. Soil besides containing a mixture of clay minerals also may have a variety of minerals like quartz, feldspars, micas and amphiboles or pyroxenes in different proportions. In such a case all these constituent minerals may have their own reactions with hydrated lime and interpretation of the end product in terms of the process becomes complicated.

Two types of clay were chosen kaolinite (representing the non swelling type) and bentonite (the expansive type), so that both of them in their individual performance would finally enable us to appreciate the role of clay structure in clay-lime interactions.

Kaolinite of Saurashtra source (as supplied by M/S Industrial Minerals and Chemical Co., Bombay) has quartz as the major impurity. Bentonite of quick dispersing type of American Colloid Co. Illinois [as supplied by Soil Test Inc. (U.S.A.),] has its dominant

constituent montmorillonite and quartz as the impurity.

The grain size distribution of both these materials is indicated in Fig. 1 . The following are the Atterberg limits for these materials.

	L.L.	P.L.	P.I.	S.L.
Kaolinite	33.50	18.10	15.40	18
Bentonite	665	43.13	621.37	10

Fig. 2 represents the powder diffraction patterns for these starting materials.

Hydrated lime $\text{Ca}(\text{OH})_2$, employed in the present investigation is supplied by Comet Chemicals, Bombay and the impurities are specified to be 2 percent.

METHODS:

The bentonite and kaolinite were pulverised and passed through 100 ASTM mesh and oven dried at 110°C for 24 hours.

Lime prior to its use in the experiments was carefully sealed in individual packets and stored in dessicator to prevent carbonation.

Kaolinite - lime and bentonite - lime ^{mixtures} of various proportions as indicated subsequently were prepared by blending together appropriate amounts of these constituents in dry state. Distilled water was then added upto plastic limit and the mixing continued until a uniform mixing with the water was achieved. These mixtures were then sealed in polythene bags with wax and kept in a constant temperature room (maintained

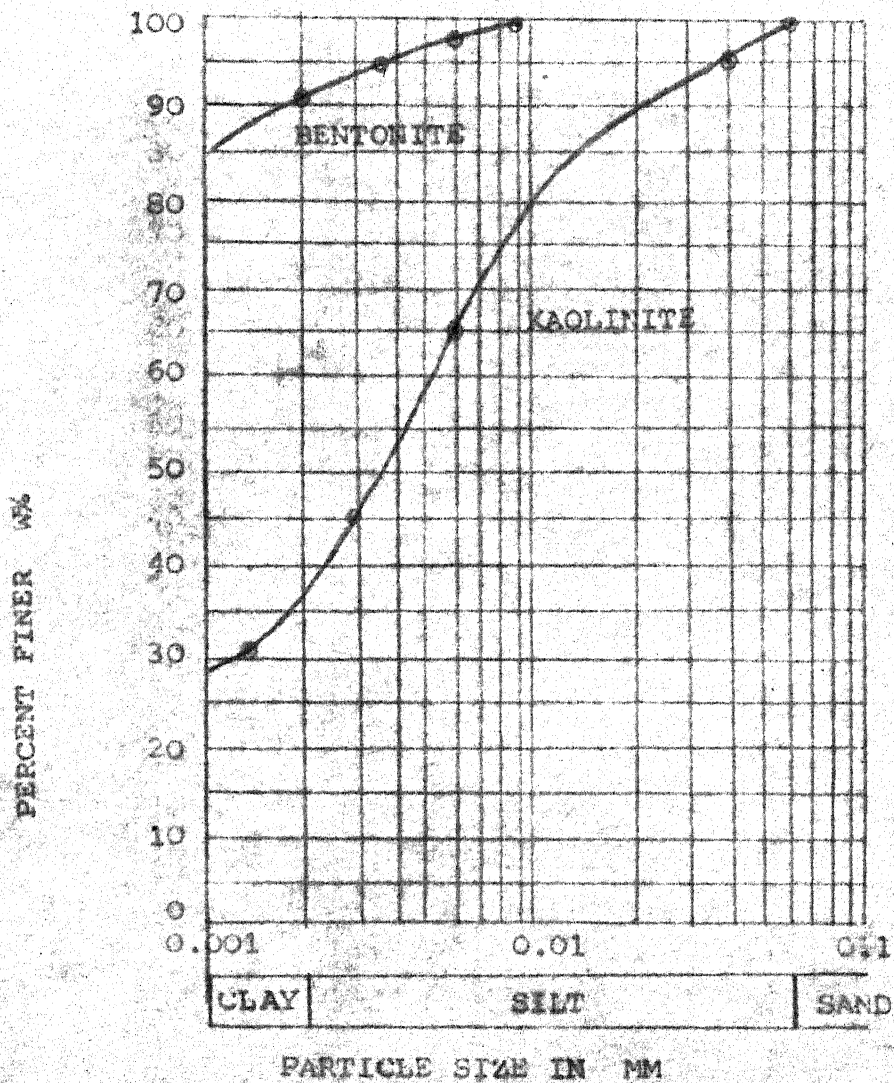
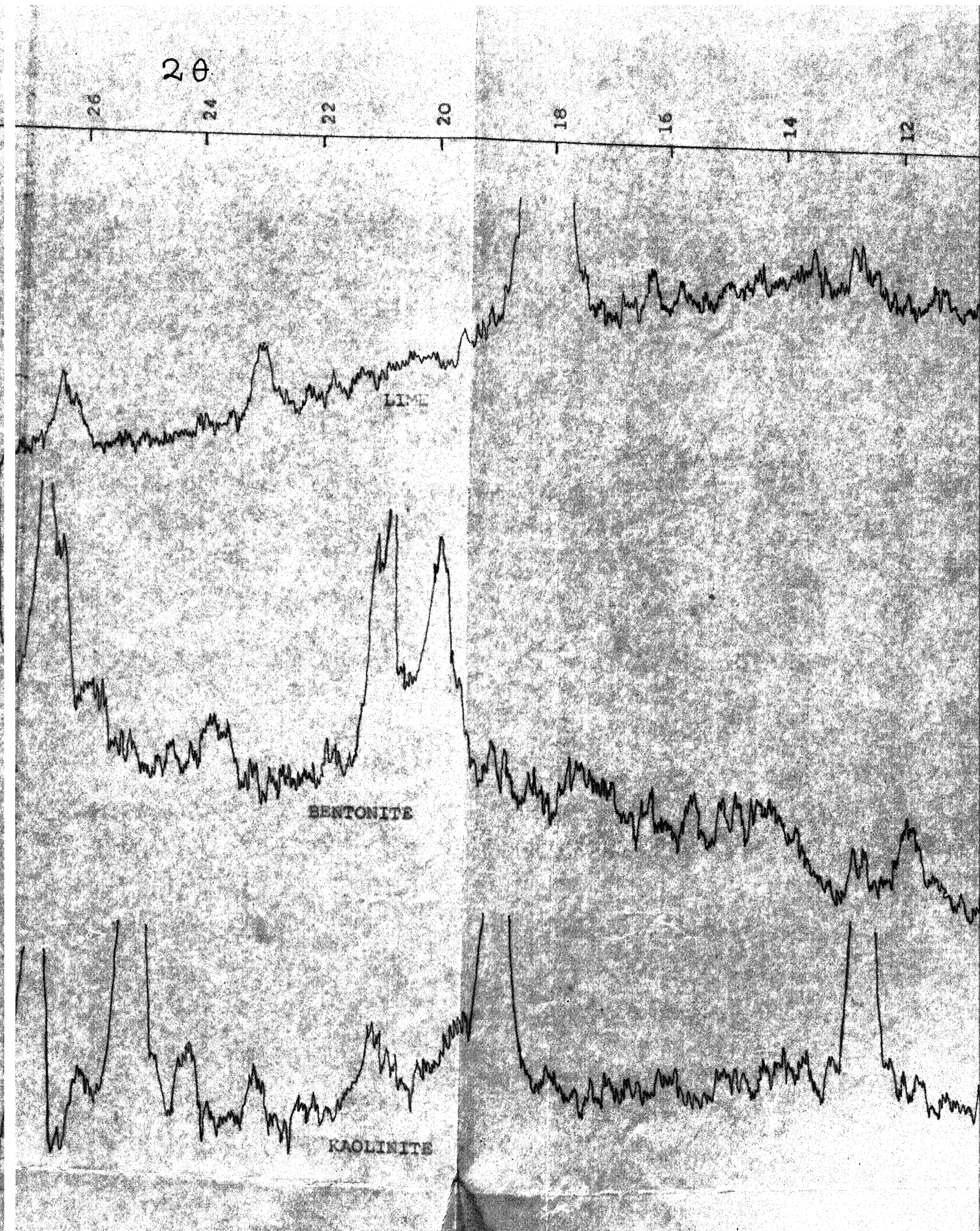
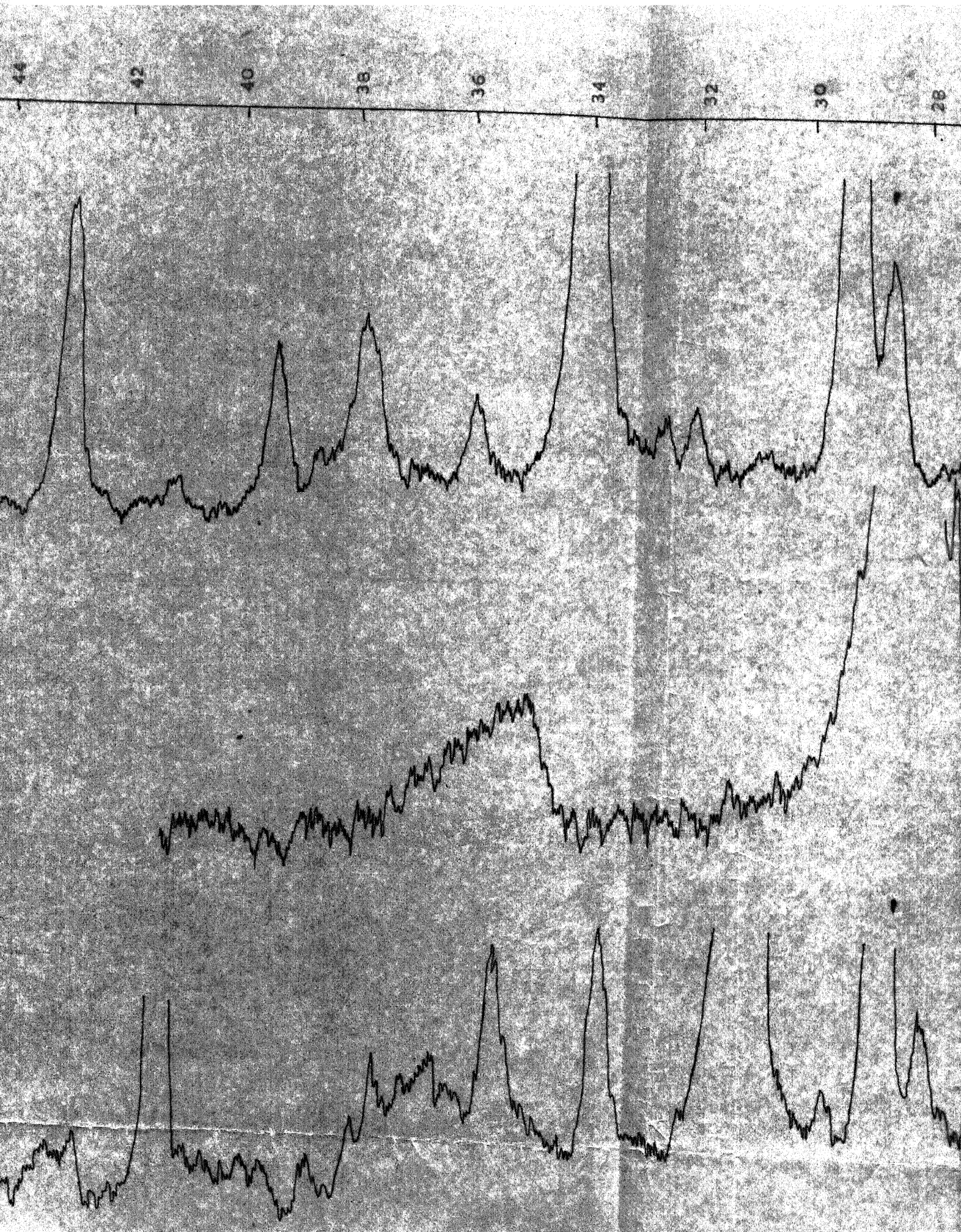


FIG. 1 GRAIN SIZE DISTRIBUTION PATTERN FOR KAOLINITE AND BENTONITE



around $70 \pm 5^\circ\text{F}$).

The Atterberg limit tests were conducted as per ASTM Standards D423-61T, D424-59 and D427-61. For all the limit tests, the final result was taken on the basis of 4 test results.

For Unconfined Compressive Strength the proving ring type unconfined compression testing apparatus was used. It is a constant strain device. The rate of strain was kept at 0.03 per minute throughout.

By static compaction cylindrical specimens of $3\frac{3}{8}$ in. long and $1\frac{1}{2}$ in. diameter were prepared taking care to ensure that the moisture content throughout the sample was kept at the plastic limit. The samples to be kept for aging were moulded in cylindrical tubes 6 in and $1\frac{1}{2}$ in diameter. After compaction the tubes were sealed at both ends by sealing wax to prevent the loss of moisture and carbonation of the lime by the carbondioxide in the atmosphere. Samples were stored in the temperature controlled room.

X-ray diffraction studies were conducted with the help of XPD-5 and XRD-6 diffractometers (of G.E.C. make) with automatic counter. Copper K_α radiation with Ni-filter was adopted with the slit width 0.1 for both the kaolinite lime and bentonite - lime samples. However for scanning (001) peak of montmorillonite, the CuK_α could not be successfully employed owing to the low angle occurrence of the peak. As such CrK_α radiation

was resorted to for scanning the montmorillonite basal peak (001) in all the samples. For CrK_α radiation $\sqrt{1}$ filter was used.

Prior to x-ray diffraction analysis the clay-lime mixtures both fresh as also after different aging periods for different lime contents were finely ground, where necessary, in an agate mortar and packed into a plexiglass sample holder.

For samples screened with filtered CuK_α radiation scanning was done in the range $5^\circ < 2\theta < 40^\circ$ at a speed of $2^\circ(2\theta)/\text{min}$ and a recording speed $2^\circ(2\theta)$ per inch.

With CrK_α , the scanning range was $5^\circ < 2\theta < 15^\circ$ with the other operational details remaining the same.

For quantitative representation of the test data, the integrated intensities with a planimeter were determined.

CHAPTER IV

VARIATION OF PHYSICAL PARAMETERS IN THE CLAY-LIME SYSTEM

Physical parameters in the clay-lime system are dependent on the crystal structure and composition of the clays involved. The two types of clay chosen, kaolinite and bentonite (with montmorillonite as dominant clay) have the crystal structure different. The kaolinite structure is composed of a single tetrahedral sheet and a single alumina octahedral sheet combined in a unit so that the tips of the silica tetrahedrons and one of the layers of octahedral sheet form a common layer (Fig. 3). All the tips of the silica tetrahedrons point to the same direction and towards the centre of the unit made up of silica and octahedral sheets. The distribution of the silicon, alumina, oxygen and hydroxyl in kaolinite is such that the charges within the structure ^{are} ~~and~~ balanced, that is there are no charges on the lattice due to substitutions within the lattice. Montmorillonite however is a three layered clay and is composed of units made of two silica tetrahedral sheets with a central alumina octahedral sheet (Fig. 4). All the tips of the tetrahedrons point to the same direction and towards the centre of the unit. The tetrahedral and octahedral

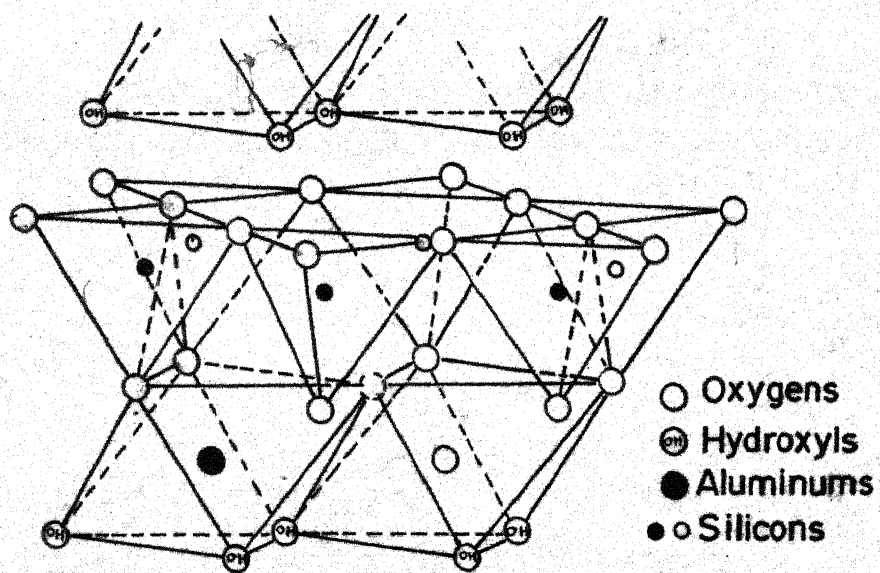


FIG. 3. DIAGRAMMATIC SKETCH OF THE STRUCTURE OF THE KAOLINITE LAYER, AFTER GRUNER. (1932)

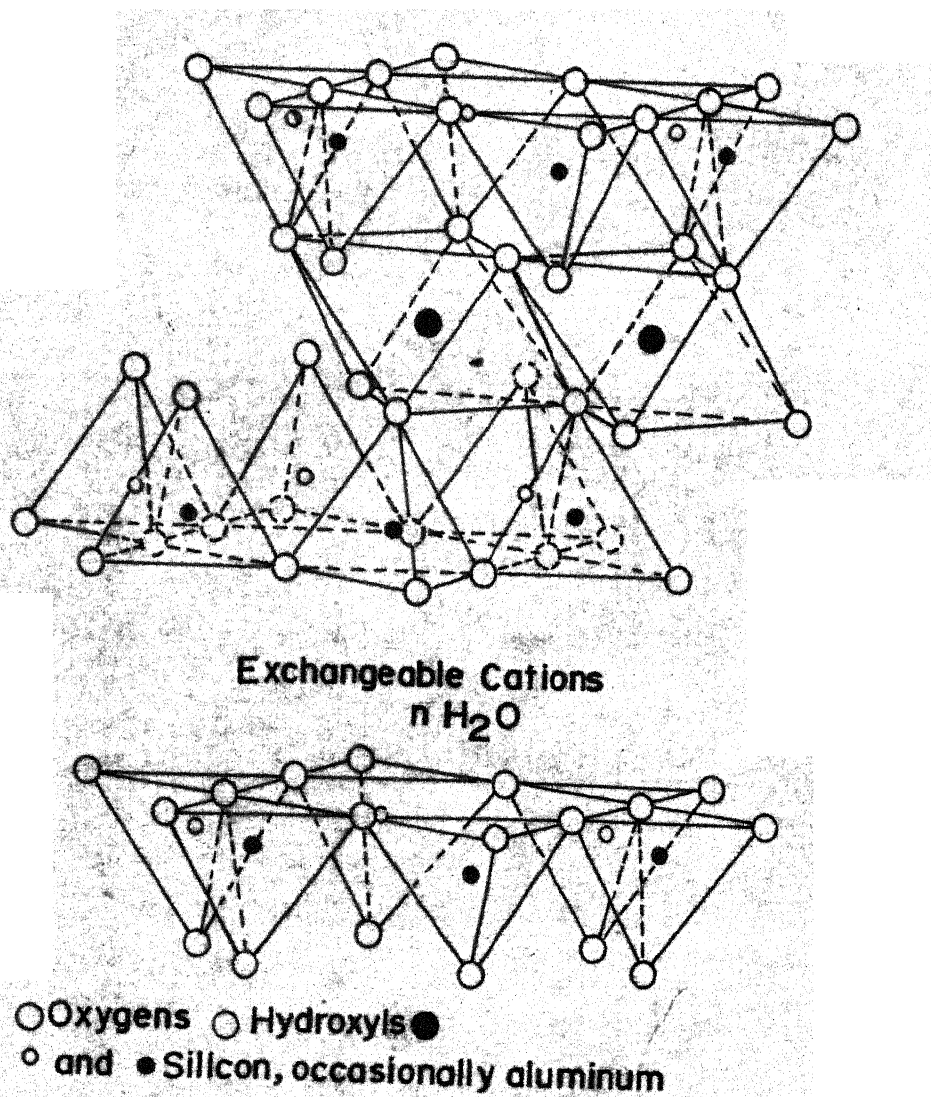


FIG. 4. DIAGRAMMATIC SKETCH OF THE STRUCTURE OF MONTMORILLONITE ACCORDING TO HOFMANN, ENDELL, AND WILLIAMS (1933, 1935, 1942).

sheets are combined so that the tips of the tetrahedrons of each silica sheet and one of the hydroxyl layers of the octahedral sheet form a common layer. The atoms common to both the tetrahedral and octahedral layer become oxygens instead of hydroxyls. Due to the stacking of oxygen layers of each unit adjacent to the oxygen layers of the neighbouring unit, the bonding is very weak and this is the reason for the entry of water and other polar molecules into the lattice consequently causing expansion of lattice in the **c**-direction.

In contrast to the kaolinite lattice, the montmorillonite lattice is always unbalanced which is generally the resultant of the substitutions of ions of different valence in the tetrahedral or octahedral sheets or both. It has been reported that the charge deficiency is about 0.66 per unit cell. This net charge deficiency is balanced by exchangeable cations adsorbed between unit layers and their edges.

During the process of clay stabilization with lime, the calcium ions of the lime that is added to the clay are potential source of satisfying the charge deficiency that might be present in these clay minerals. The calcium ions of lime can enter the clay lattice if the clay has the favourable cation exchange capacity and if such replacement is possible in the clay involved. In montmorillonite due to the net charge defic-

iciency, the adsorption of calcium ions from external environment in the clay-lime system can take place. Evidence (cited in the next chapter) have clearly indicated this possibility in the Sodium montmorillonite of the present study. In case of kaolinite, even though theoretically the lattice is a balanced one, broken bonds due to lattice distortions and around the edges of the silica-alumina units give rise to unsatisfied charges which have to be balanced by adsorbed cations. The rate of adsorption in kaolinite is lower than in the montmorillonite lattice. It is this nature of cation and the extent of adsorption that influence the water retention property in these two clay types.

In the present study, the consistency limits (liquid limit, plastic limit and shrinkage limit) and strength parameter (Unconfined compressive strength) have been determined. The variations of these parameters for different lime levels in both types of clay and at different aging periods of time are graphically represented.

I ATTERBERG LIMITS FOR THE LIME-CLAY SYSTEMS:

LIQUID LIMIT:

Fig. 5a represents the variation of liquid limit of kaolinite with different percentages of lime. The addition of lime brought about an increase of the liquid

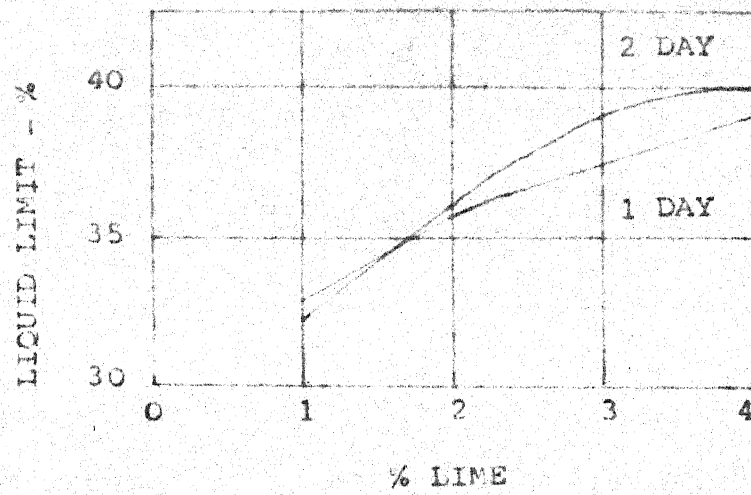


FIG. 5(a) LIQUID LIMIT CHANGES WITH INCREASING LIME CONTENT IN KAOLINITE-LIME SAMPLES

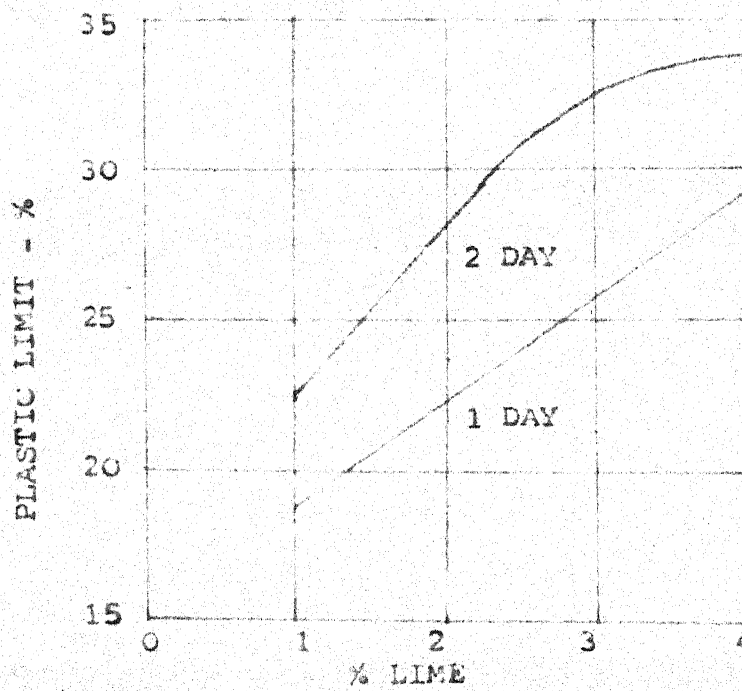


FIG. 5(b) PLASTIC LIMIT CHANGES WITH INCREASING LIME CONTENT IN KAOLINITE-LIME SAMPLES

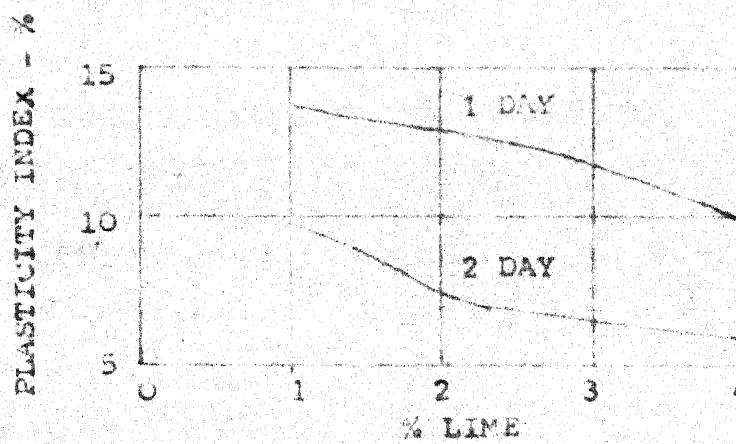
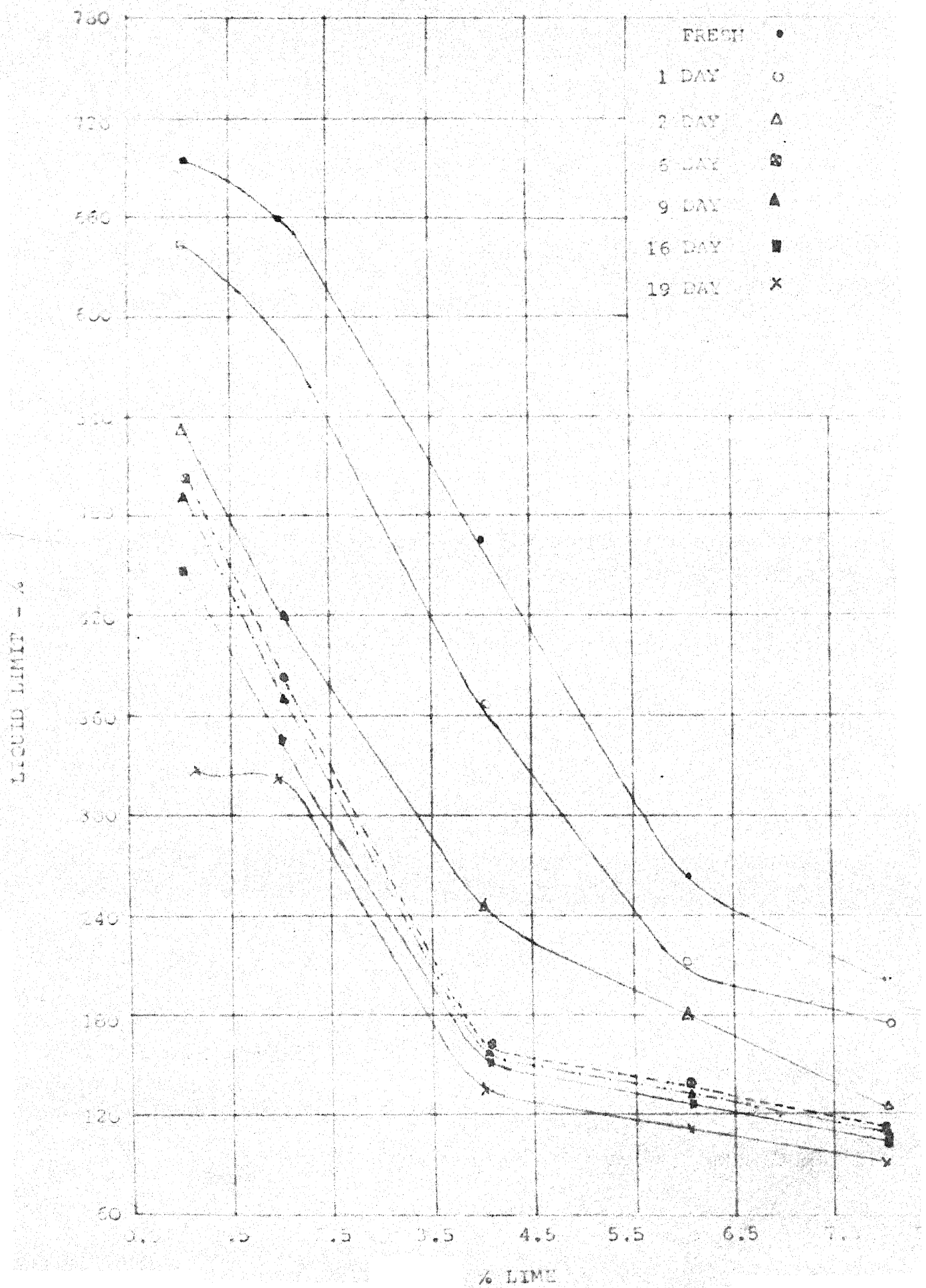


FIG. 5(c) PLASTICITY INDEX CHANGES WITH INCREASING LIME CONTENT IN KAOLINITE-LIME SAMPLES

limit values. The rate of increase was higher for the initial 2 percent addition of lime and then subsequently the rate falls to a certain extent but still the limits are in an increasing trend.

In contrast to this, the liquid limit behaviour in bentonite is very characteristic. There is a general decrease, with increasing lime, for liquid limit in case of bentonite. For any particular lime level with aging further decrease of the liquid limit was noticed. Fig.7 indicates the liquid limit variation in bentonite. As can be noticed from the figure, the rate of decrease was faster upto 4 percent of lime in the system and beyond which level, the decrease is at a slower rate. This appears to be quite striking. It is also seen that the rate of change of the liquid limit for bentonite is higher with increase of lime than that for kaolinite in the same lime level. This is due to the activity and higher cation exchange capacity of bentonite. While this break in the rate of variation is at 2 percent lime level in kaolinite, it is at 4 percent lime level in bentonite indicating that the adsorption of calcium ions has taken place substantially in bentonite upto 4 percent of lime addition into the system. This decrease in liquid limit is in consonance with the reported observations by Wang et al (1963), Jan and Walker (1963) and Katti et al (1966). But no



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IN BENTONITE-LIME SAMPLES

attempt however has been made to explain the reason.

The liquid limit variations can be explained as follows: The exchangeable cations are not all held in a layer right at the clay surface but are situated at some average distance from the surface. Though the electrical force between the negatively charged surface and positively charged ions attracts the cations to the surface, their thermal energy tends to diffuse them away. The balance of coulomb electrical attraction and thermal diffusion leads to a diffuse layer of cations, with the concentration highest at the surface and gradually decreasing with distance from the surface. This concept, popularly known as "diffuse double layer" involves one layer of negative charges in the clay layer at the surface and other layer being the diffuse layer of cations balancing the negative charge.

The interparticle forces of attraction and repulsion and the net force in the system depend on the charge distribution in the clay and the nature of cation involved. Repulsion results from interpenetration of diffuse ion-layers of adjacent particles and from adsorption of water on surfaces of adjacent particles. This repulsion will be greatest with monovalent exchangeable ions. The force of attraction is from different sources - (a) the attraction bet-

ween molecules and atoms (described by London - Vander Walls Theory). These decrease vary rapidly with short increase in distance of separation. (b) Coulomb force of attraction (inversely proportional to the square of the distance), (c) other ~~for~~ces of attraction due to bonding material.

These interparticle forces have a significant role in determining the liquid limit. The distance between particles, or between structural units of particles, is such that the forces of interaction between the clay particles become sufficiently weak to allow easy movement of particles relative to each other. The cohesion between the particles is small. In bentonite (swelling type of clay), the dominant interparticle force is one of repulsion. This force of repulsion determines the distances between particles. Therefore, an increase in calcium concentration that is substitution of divalent Ca - ion for monovalent exchangeable cations in bentonite decrease repulsion and hence the decrease of liquid limit noticed in the present study.

In kaolinite however, the increase of liquid limit with increase of lime in the kaolinite - lime system is quite characteristic and to certain extent a deviation from normal behaviour of any clay. Clare and Crouchley (1957) reported a drastic increase in

the liquid limit of a clay saturated with Ca - ions in its natural state. According to them, this behaviour is typical in clay - lime interaction of any clay that has calcium enrichment in its composition. Diamond and Kinter (1966) observed that mixtures of lime and calcium saturated clay assume an increasingly dry appearance. Sometimes the reaction is so extreme that a free-flowing slurry mixture may stiffen so that it will no longer pour. This reaction would be reflected by an increase in the liquid limit. Generally the liquid limit seems to increase on the addition of lime when there is no specific tendency in the opposite direction created by cation exchange effects. In the present investigation also, the starting material was a calcium rich kaolinite.

PLASTIC LIMIT:

The variation of plastic limit with increasing lime content in clay-lime systems and effect of aging to different periods of time of these systems on plastic limit is indicated in Figures 5b and 8. It is noticed that plastic limit increases with increasing lime content in both the clays. Effect of aging appeared to be the increase of plastic limit for any lime level in the clay - lime system. On aging to sufficiently longer time, say for 16 to 19 days, it was observed that the rate of increase of plastic limit

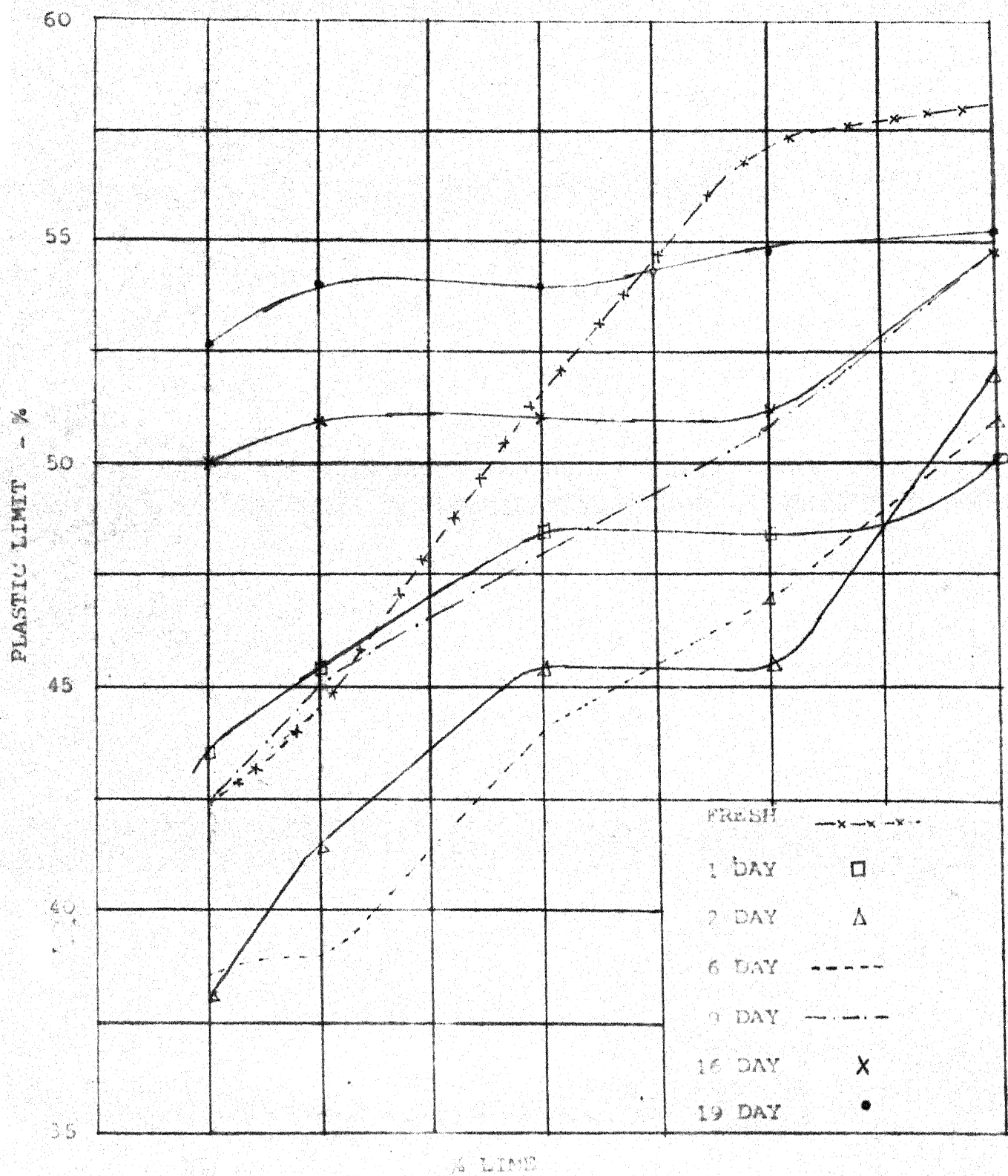


FIG. 8 PLASTIC LIMIT CHANGES WITH INCREASING LIME CONTENT IN BENTONITE-LIME SAMPLES

in bentonite changes and becomes slower even at 2 percent lime. This indicates that even with 2 percent lime, on aging to 16 or 19 days in bentonite the changes that take place might be responsible for this modification in the hydration pattern of bentonite. The increase of plastic limit has been reported by Diamond and Kinter (1966), Scott (1965), Katti et al (1966).

The plastic limit determination involves rolling of the sample that induces relative movement of particles which take new positions retaining the equilibrium. The movement of the particles is largely dependent on the nature of bonding and amount of water present. Sufficient water is required to wet all the surfaces and minute pores. When lime is added, calcium ions cause a change in the electrical charge density around the clay particles that affect flocculation or aggradation. The clay particles now acting as aggregates behave as a silt which has low cohesion.

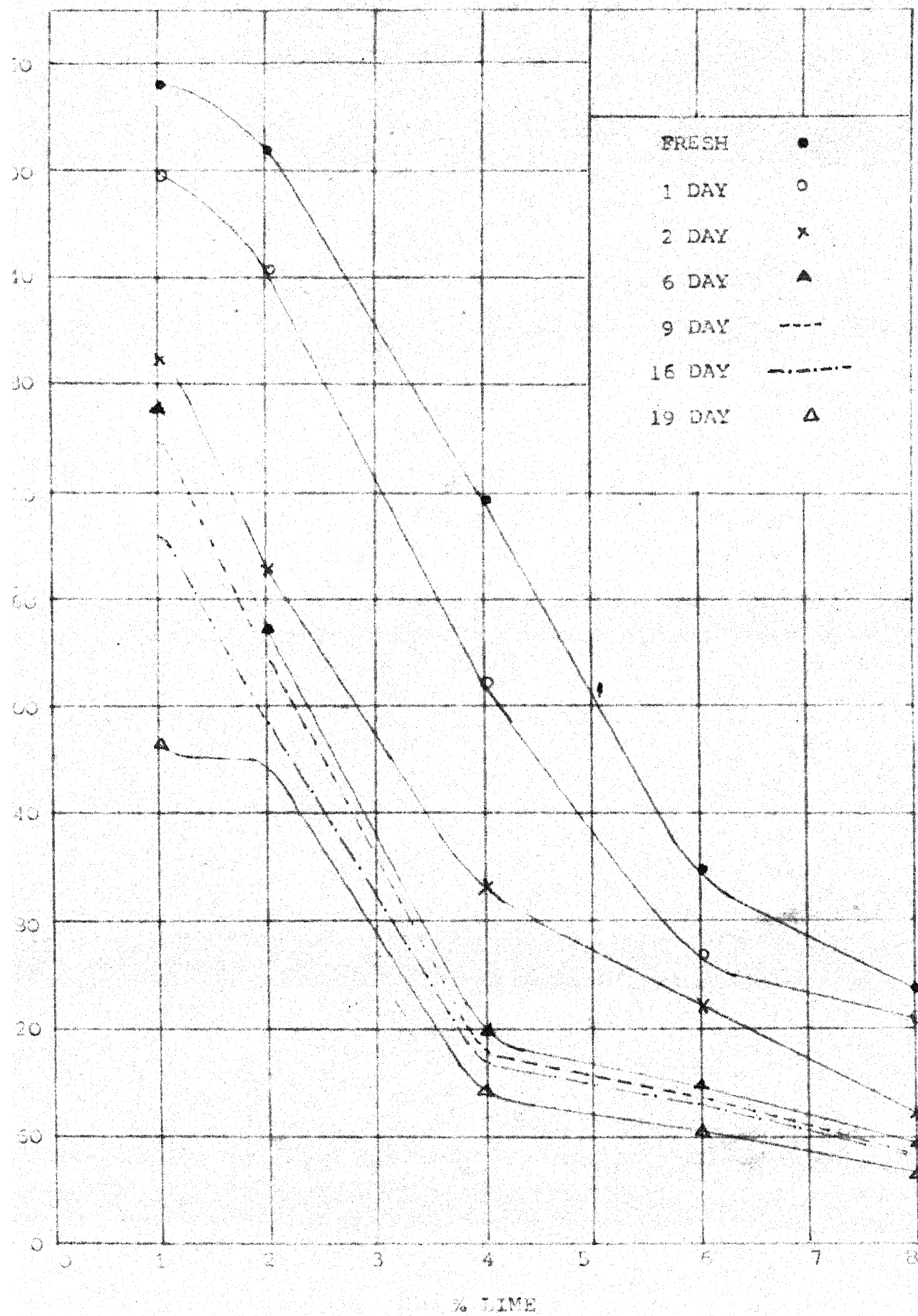
The plastic limit is the lowest moisture content at which the bonds between soil particles or aggregates can be constantly renewed (Hilt and Davidson, 1960). The nature of these bonds has been described as being due to cation exchange and to a crowding of additional cations on to the surface of the clay (Davidson and Handy 1959). The surface tension of water in minute pores in clay also exerts a bonding force between

clay particles. Because capillary pressure is inversely proportional to the radius of curvature of the meniscus and directly to the surface tension, changes in either of these will be reflected in the amount of water necessary to renew the bonds continually between soil particles while a plastic limit is being rolled.

When the plastic limit of clays ~~has~~ increased with the addition of lime, actually more water must be added to the clay-lime system to make the bonds between the clay particles capable of being renewed as rapidly as they are broken. Due to flocculation and aggregation, though the bonding between the particles within a floc has been increased, bonding between the flocs is relatively weak.

PLASTICITY INDEX:

The plasticity index values for various kaolinite-lime and bentonite-lime systems are represented in Figures 5c and 9. The general decrease of the plasticity index for both these cases is characteristic. In spite of the increase of liquid limit for kaolinite, the increase is not as large as the accompanying increase in plastic limit. The separate effects of the addition of lime to clay on the liquid and plastic limits combine to result in a rather sharp decrease in the plasticity index. Such variation was also been reported by Diamond and Kinter (1966).



SHRINKAGE LIMIT:

For kaolinite - lime system as well as bentonite - lime system, a general increase of shrinkage limit takes place with increasing lime additives (Figures 6 and 10). However in case of kaolinite, the increase was only significant upto 2 percent of lime after which, the rate of increase of shrinkage limit appears very low. This indicates the effect of adsorbed lime and is in consonance with a similar trend noticed in the liquid limit variation. For bentonite however, upto 4 percent of lime the shrinkage limit variation is pronounced but even with higher percentages of lime there is not much of a deviation from this rate. The effect of aging in both these cases was to enhance the shrinkage limit values.

Shrinkage limit value for any clay depends on its activity. Increase in activity of a clay increases its uptake of water during hydration. The dehydration patterns also are dependent on the hydration mechanism. For example, montmorillonite that takes maximum water during hydration (as in the case of Na - variety) has the lowest shrinkage limit. With increasing Ca - ions adsorption, bentonite hydration characteristics change as the activity of bentonite falls down. According to Skempton (1953), the activity of Sodium montmorillonite is 7.2 while for calcium

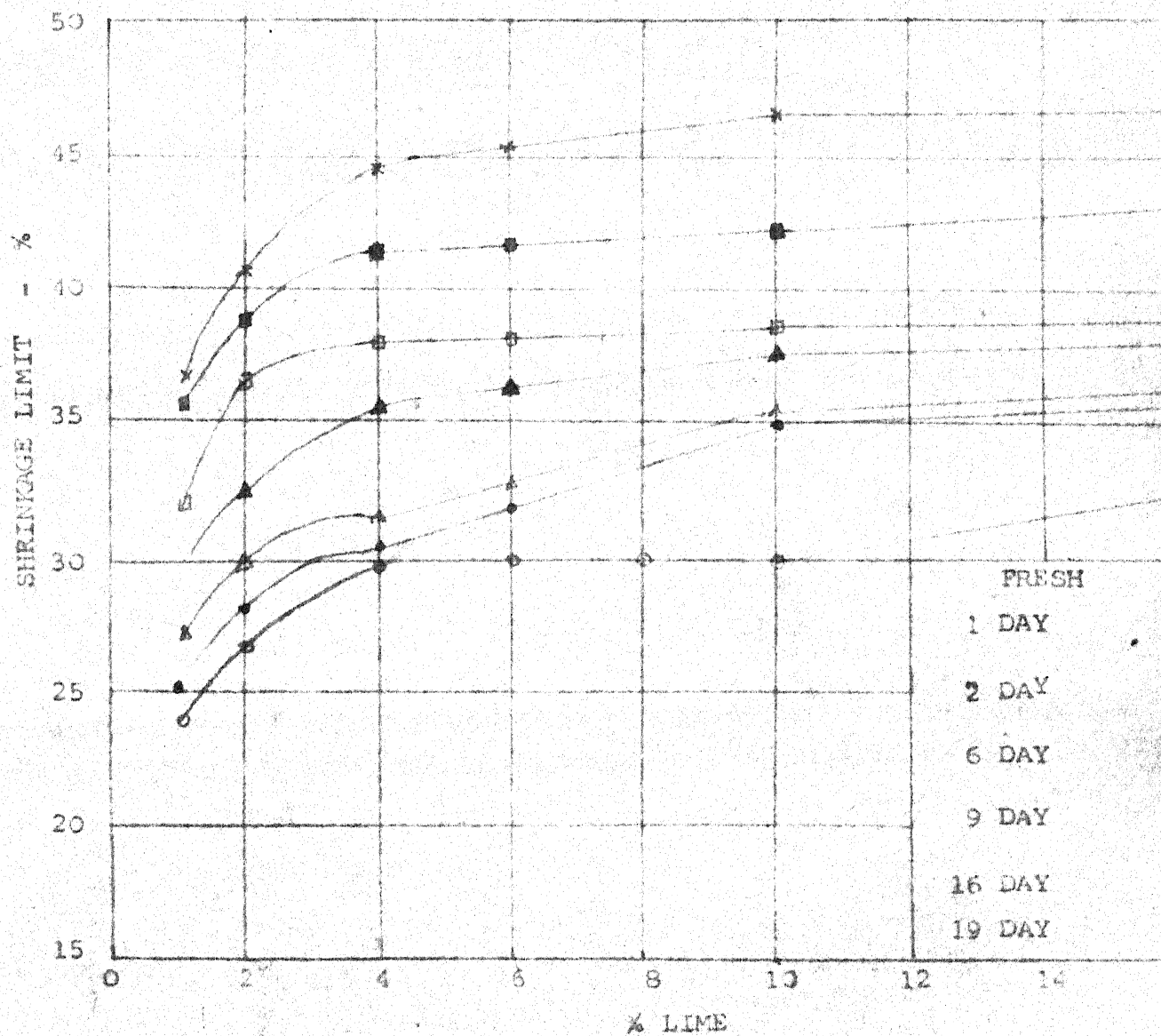


FIG. 6 SHRINKAGE LIMIT CHANGES WITH INCREASING LIME CONTENT
LIME SAMPLES

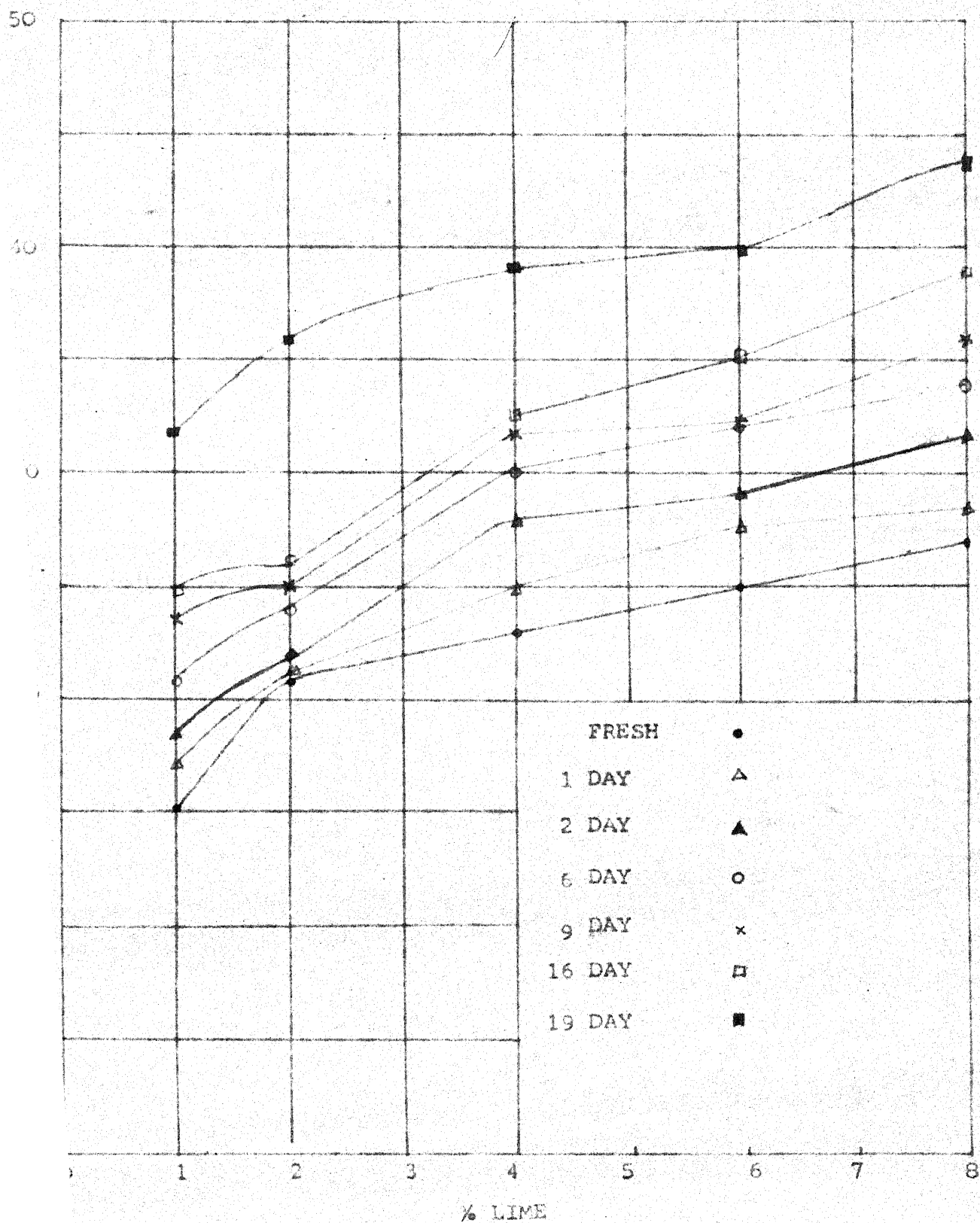


FIG. 10 SHRINKAGE LIMIT CHANGES WITH INCREASING LIME CONTENT IN BENTONITE-LIME SAMPLES

montmorillonite it is about 1.5. This decrease in activity tends to raise the shrinkage limits as observed in the present case. The increase is limited in kaolinite because of limited adsorption of Ca-ions from Ca(OH)_2 added, while with montmorillonite it is remarkable.

Strength properties:

The unconfined compressive strengths for the kaolinite-lime and bentonite - lime systems were determined on fresh system with different lime levels as also the same in aging to different days. For bentonite, the strength instantaneously starts increasing upto about 2 percent at a rapid rate and then the increasing tendency continuing further upto 6 percent of lime but at a slower rate. Beyond 6 percent of lime, the strength falls down.

For kaolinite, there is a rapid increase of strength upto 2 percent lime and then fluctuations of strength, ^{takes place} till 10 percent lime and beyond 10 percent a distinct increase in strength is noticed (Figures 11 and 12).

The strength variation in these two clays is dependent on many factors that emerge during the stabilization process. The reaction of a clay mineral to Ca(OH)_2 is based on the structural setup of the clay. In kaolinite, the charge deficiency being

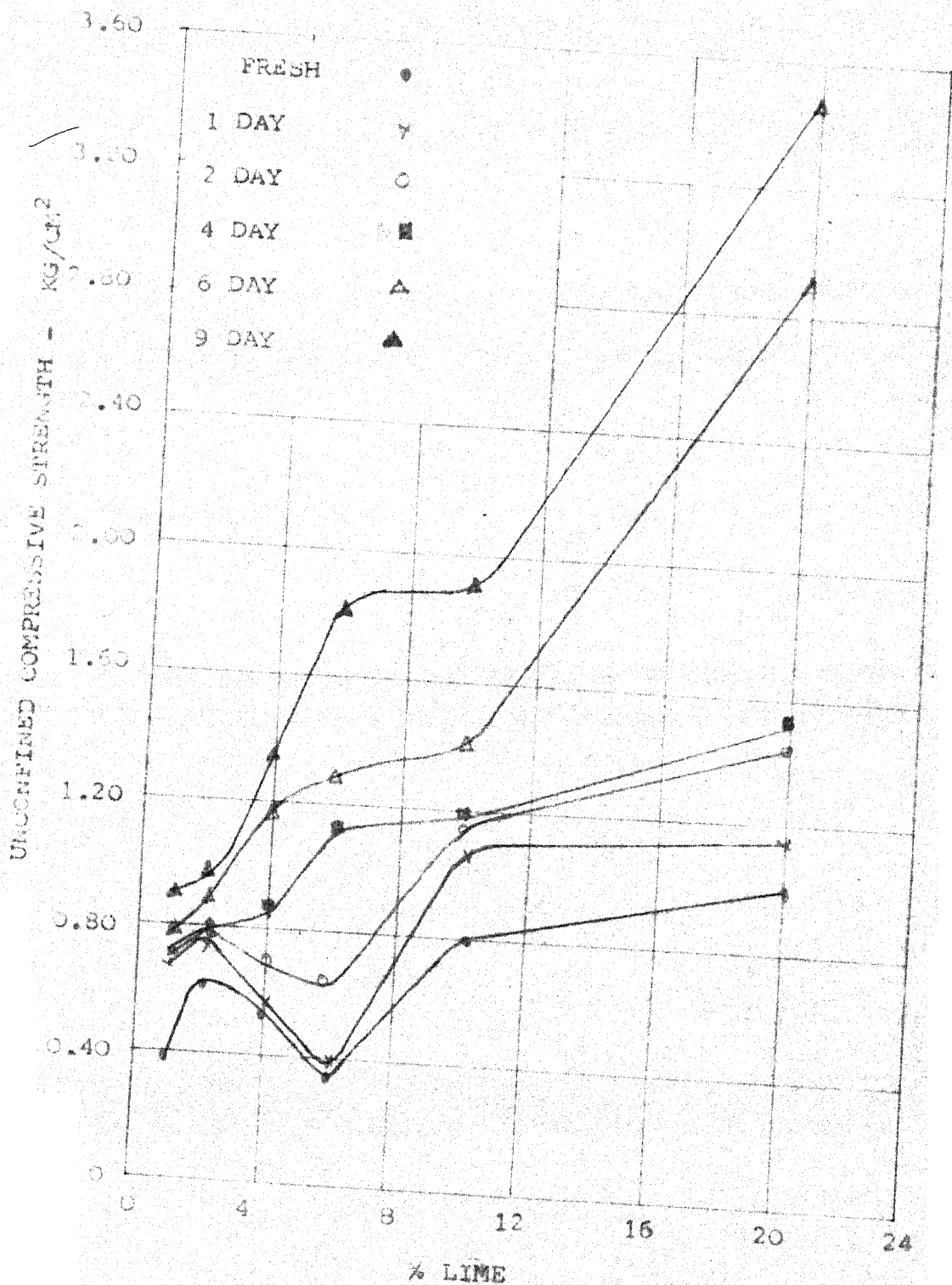


FIG. 11 EFFECT OF AGING ON UNCONFINED COMPRESSIVE STRENGTH FOR KAOLINITE-LIME SAMPLES WITH VARIOUS LIME LEVELS

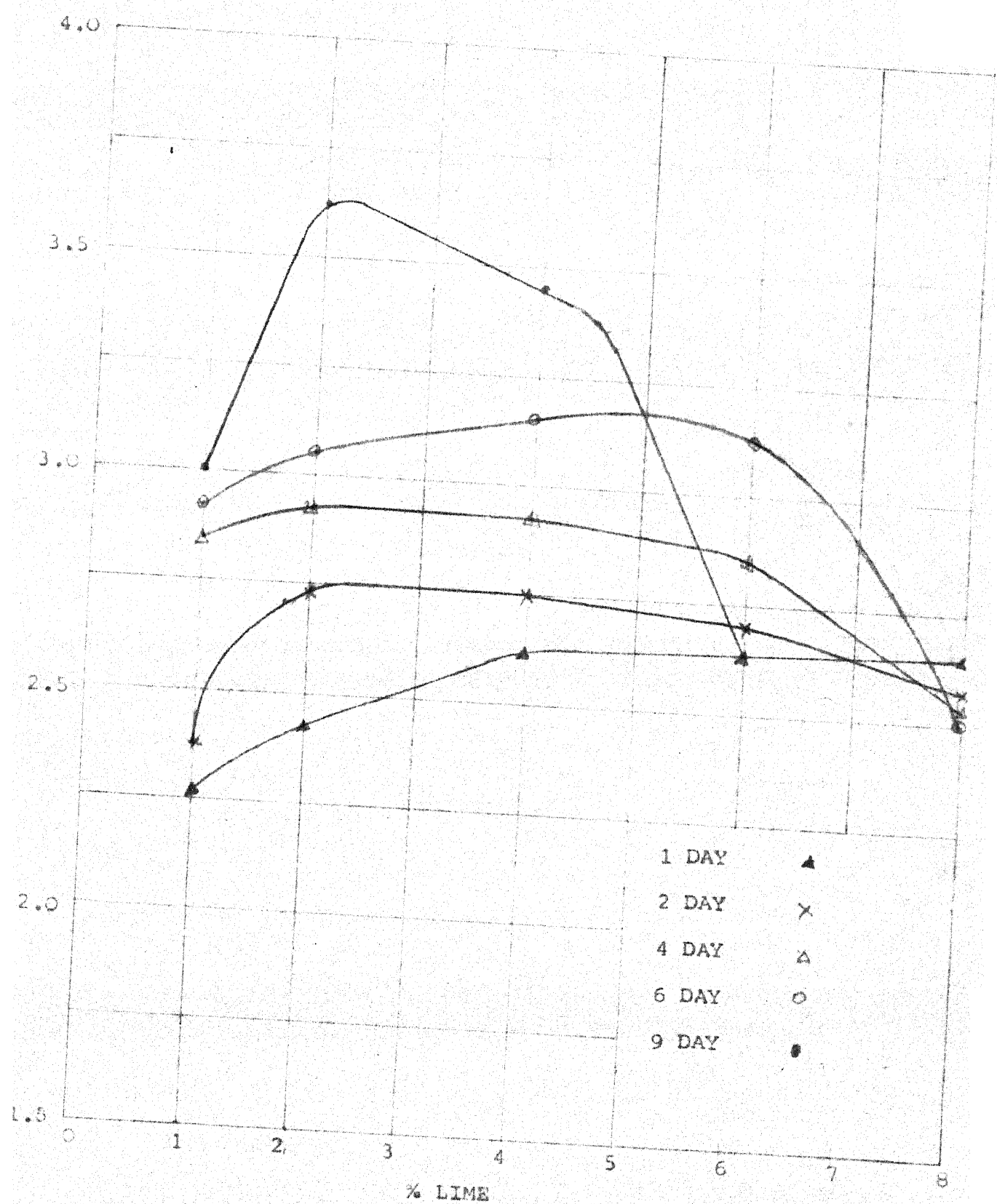


FIG. 12 EFFECT OF AGING ON UNCONFINED COMPRESSIVE STRENGTH FOR BENTONITE-LIME SAMPLES WITH VARIOUS LIME LEVELS

very low, the adsorption of Ca-ions would be restricted (upto about 2 percent in the present case) and the rest of the lime would start attacking the kaolinite minerals and trying to break chemically the bonds at every stage instantaneously. During this time a gel - like silicate starts forming which is of course very difficult to be tracked by X-ray diffraction techniques. This reaction seems to take place by lime eating around the edges of kaolinite particles with a new phase forming around the core of the unaltered kaolinite (Grim 1960). While Grim reports an immediate rise with the first increment of lime in the unconfined compressive strength, the present investigation reveals that the immediate rise is only upto 2 percent lime and when the Ca-ions adsorption stops at this stage (as is reflected in the other limit tests) in the kaolinite - lime system, the gel like material that starts forming would reduce the strength immediately on precipitation from reactions. However, on aging when the gel - like material crystallizes (for example at 6 percent lime level but after 2 days of aging), this decrease is not noticed. Hence it appears that with prolonged aging between 2 to 10 percent lime level the build up in strength of the system is quite significant (Figure 11). Beyond 10 percent lime, the strength increment though present

is not conspicuous and at a slower rate except for longer periods of aging. During this stage, the new crystalline silicates (described in detail in the subsequent chapter) as evidenced from x-ray data forms a cementing and bonding material between the clay particles and hence the strength increment.

In contrast to the kaolinite the reaction of lime with three-layered clay minerals begins by a replacement of the existing cations between the silicate sheets with Ca-ions. Following the saturation of the interlayer positions with calcium, the whole clay mineral structure deteriorates without the immediate formation of substantial new crystalline phases (Grim 1960). In case of bentonite which has a high cation - exchange capacity, an appreciable amount of lime is required to drive the calcium on to and into the clay. Rapid increase in strength upto 4 percent is due to the adsorption of Ca-ions into clay lattice and onto the surface. It is a known fact that in a material where monovalent ions like Na^+ are replaced by divalent ions like Ca^{++} (both having almost the same ionic radii), the net increase in ionic bonding ensues. The consequent increase in the strength of the system results. With the rate of adsorption of Ca-ions decreasing in the system (which is beyond 4 percent of lime as evidenced

from the other data as discussed earlier in this chapter) the formation of hydrated calcium silicates and calcium aluminates affect the strength. However the decrease of strength in the initial stages of such a reaction due to gel formation is not evidenced in case of bentonite as the adsorption of Ca-ions, though at a slower pace continues and overlaps with the gel formation, ^{thus} the resultant effect of these two on the strength is only ^{evidence)} induced in the system behaviour (Fig.12). The 6 percent lime limit appears to be the optimum intake for bentonite as seen from Figure 12. Beyond this, the excess lime that goes with the system stays mostly as free lime with the exception of the part of lime that is consumed into reaction and formation of calcium silicates with free silica and bentonite.

At higher percentages of lime, the strength behaviour in a clay-lime system depends on the nature and extent of several constituents present in the system. The various constituents present in different quantities (details presented in the following chapter) are the unreacted clay (kaolinite or bentonite), partly reacted clay, free silica, calcium silicates formed either by reaction of Ca(OH)_2 and free silica or by reaction of lime with clay and the residual lime present. The dilution of strength, as such is a

dependent phenomena on all these complex constituents as reflected in the figures 11 and 12 for kaolinite - lime and bentonite-lime systems.

The effect of aging in kaolinite-lime or bentonite lime systems in general is to set these reactions with lesser lime levels. In kaolinite, the crystallization of gel - like silicates with aging results in the strength decrease as seen with system upto 2 days between 2 to 10 percent lime levels. In bentonite - lime system, the effect of aging is to bring the fall in strength even with 2 percent of lime if aged to 9 days. The decrease in strength beyond 6 percent lime, takes at a rapid rate with prolonged aging periods of time (4 or 6 days) as shown in figure 12.

CHAPTER V

X-RAY DIFFRACTION STUDIES

X-ray diffraction studies have been undertaken with XRD-5 and XRD-6 diffractometers (G.E.C. make) with CuK_α and CrK_α radiation. The various samples with different percentages of lime for kaolinite - lime and bentonite - lime systems were screened. Intensity calculations for specific peaks of different constituents were represented by areas of the respective strong lines.

The clay - lime stabilization process involves chemical reactions and possible formation of products at the expense of the participating constituents. The clay minerals used in this study are kaolinite and bentonite as stated earlier which have been found to contain silica evidenced from the diffraction pattern for the starting materials (Fig. 2). As such whatever chemical reactions are visualized during the short term stabilization process, they may also have this free silica (present in clay) participating in them.

The X-ray diffraction investigations have been undertaken with the following intentions:

- (a) To determine the rate of consumption of free silica in different clay - lime systems for various aging periods,

- (b) To quantitative evaluate the changes that might be possible in the clay lattice at different lime levels,
- (c) To estimate quantitatively the rate of kaolinite or bentonite consumption with the onset of reactions,
- and (d) Identification and correlation of the growth of new minerals during these reactions with the rate of depletion of constituents involved.

The various minerals involved in the present study during the stabilization are kaolinite, montmorillonite, free silica, excess lime, different new products like hydrogarnets, tetra calcium aluminate hydrates and calcium silicate hydrates. Table 1 indicates the lines that are made use of in intensity calculations and rate curves for these various constituents.

TABLE 1

LINES CHOSEN FOR INTENSITY CALCULATIONS OF THE MATERIALS INVOLVED IN CLAY-LIME REACTIONS

Material	λ 2	λ d	λ hkl
Montmorillonite	8.60	15.27	001
Kaolinite	12.45	7.10	001
Prehnite	19.30	4.59	100
Silica	26.70	3.33	101

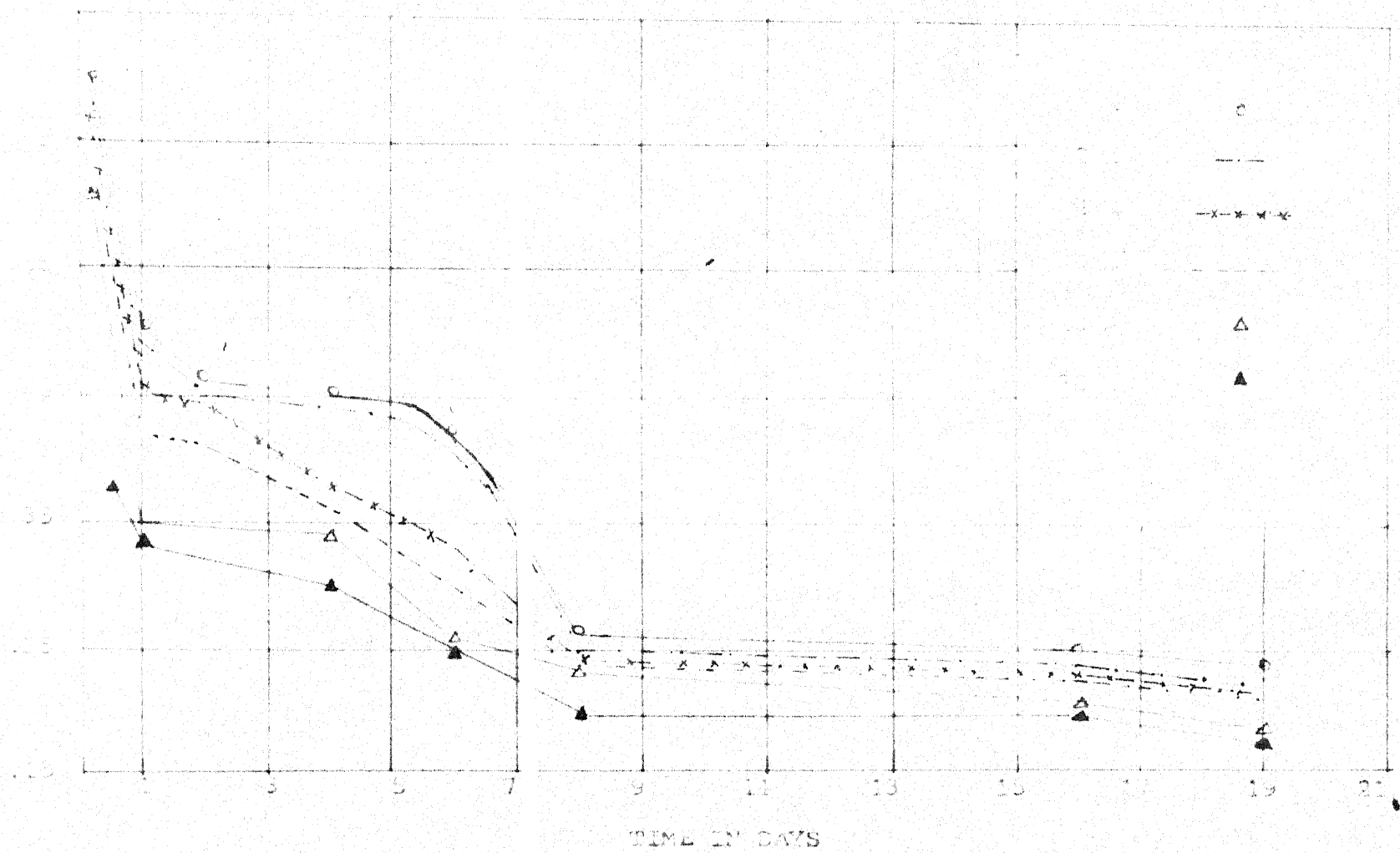


FIG. 10 CHANGE IN INTENSITY OF (001) LINE OF KAOLINITE ON AGING IN KAOLINITE-LIME SAMPLES AT VARIOUS LIME LEVELS

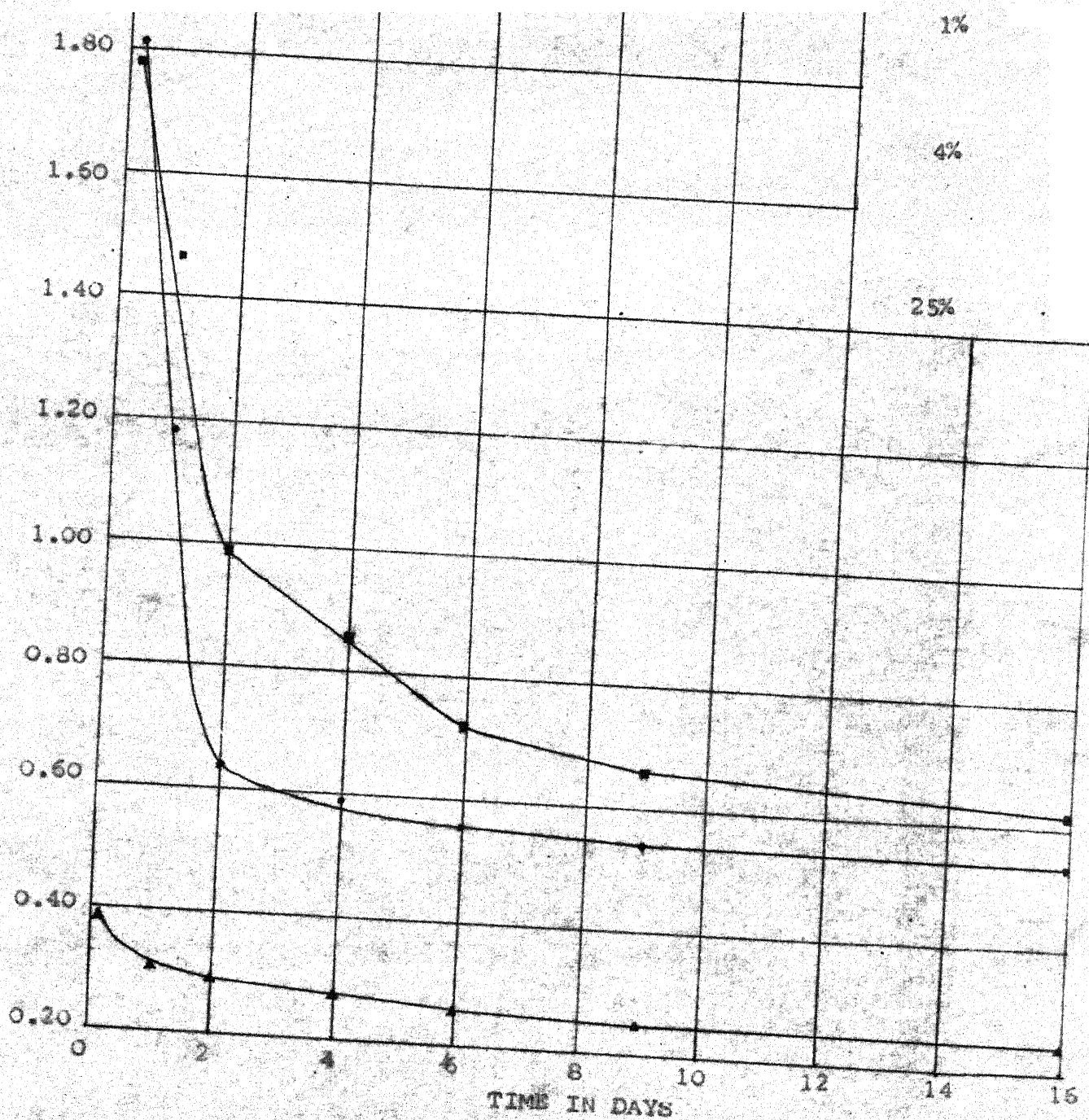


FIG. 17 CHANGE IN INTENSITY OF (001) LINE OF BENTONITE ON AGING IN BENTONITE-LIME SAMPLES AT VARIOUS LIME LEVELS

NATURE OF THE VARIATIONS FOR DIFFERENT CONSTITUENTS INVOLVED IN CLAY-LIME REACTIONS:

(1) Kaolinite: The 001 peak for kaolinite which is the strongest has been chosen to represent its quantitative involvement at various stages during the process. Figure 16 represents the change in intensity of 001 line for kaolinite with time of aging at various lime percentages in the clay - lime system. As can be seen from the figure, upto about 8 days the decrease in intensity is significant and that between the first 24 hours in all the samples the decrease is very rapid. However beyond 8 days, there seems to be a stability attained in the reaction and the rate of change is very small. It has been observed that during the first 24 hours the rate of fall is primarily due to the formation of prehnite (hydrated Calcium - aluminate - silicate). Subsequent changes might be attributed to the formation of other compounds like tetra-calcium aluminate hydrates, hydrogarnets in addition to prehnite, discussed in detail in the succeeding pages. The slow pace of changes beyond 8 days indicating the near cessation of the chemical reactions during short term aging has been further confirmed from the figure 18 which shows a similar trend in the formation of prehnite.

(2) Bentonite: The changes in intensity of 001 line of bentonite (obtained from CrK_α radiation) with

the aging time for different percentages of lime are presented in Figure 17. The initial changes in intensity upto 6 days has been primarily due to the rapid growth of a hydrated calcium aluminium silicate with a strong line at 4.43 \AA . This has also been evidenced from Figures, 19,21,23, 25 and 27 where the simultaneous changes in the bentonite and the neighbouring 4.26 \AA for this compound are characteristic. The changes from about 6 days in all the samples were possibly due to the formation of other compounds such as calcium silicate hydrates and tetracalcium aluminate hydrates.

In addition to the depletion of montmorillonite that has been accounted for so far, a significant change in the nature of the characteristic montmorillonite lines is strikingly seen (Fig. 20,22,24, 26 and 28).

The broadening of the montmorillonite peaks at 2.50 \AA is due to the adsorption of calcium into the montmorillonite lattice and the consequent lattice modifications. A tendency to reach a stability in reaction is seen in the rate curves beyond about 9 days when the reactions continue at a slower pace.

(3) Changes in the free silica line: The possibility that free silica might also contribute to the formation of new compounds was confirmed by plotting rate of change of 3.33 \AA line for silica with time of aging with several lime percentages (Fig.13 and 14).

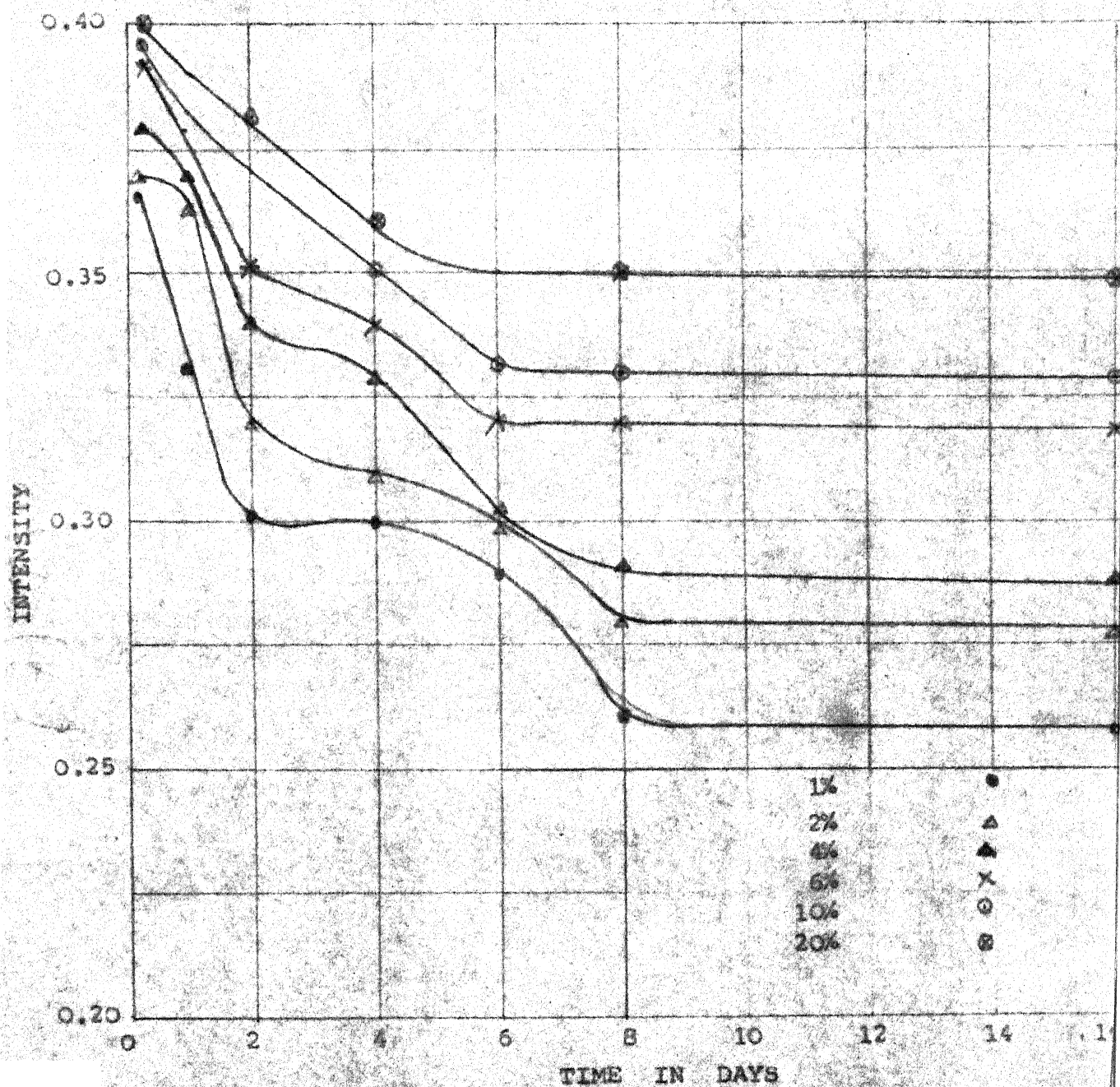


FIG. 13 CHANGE IN INTENSITY OF SiO_2 LINE OF KAOLINITE ON AG KAOLINITE-LIME SAMPLES AT VARIOUS LIME LEVELS

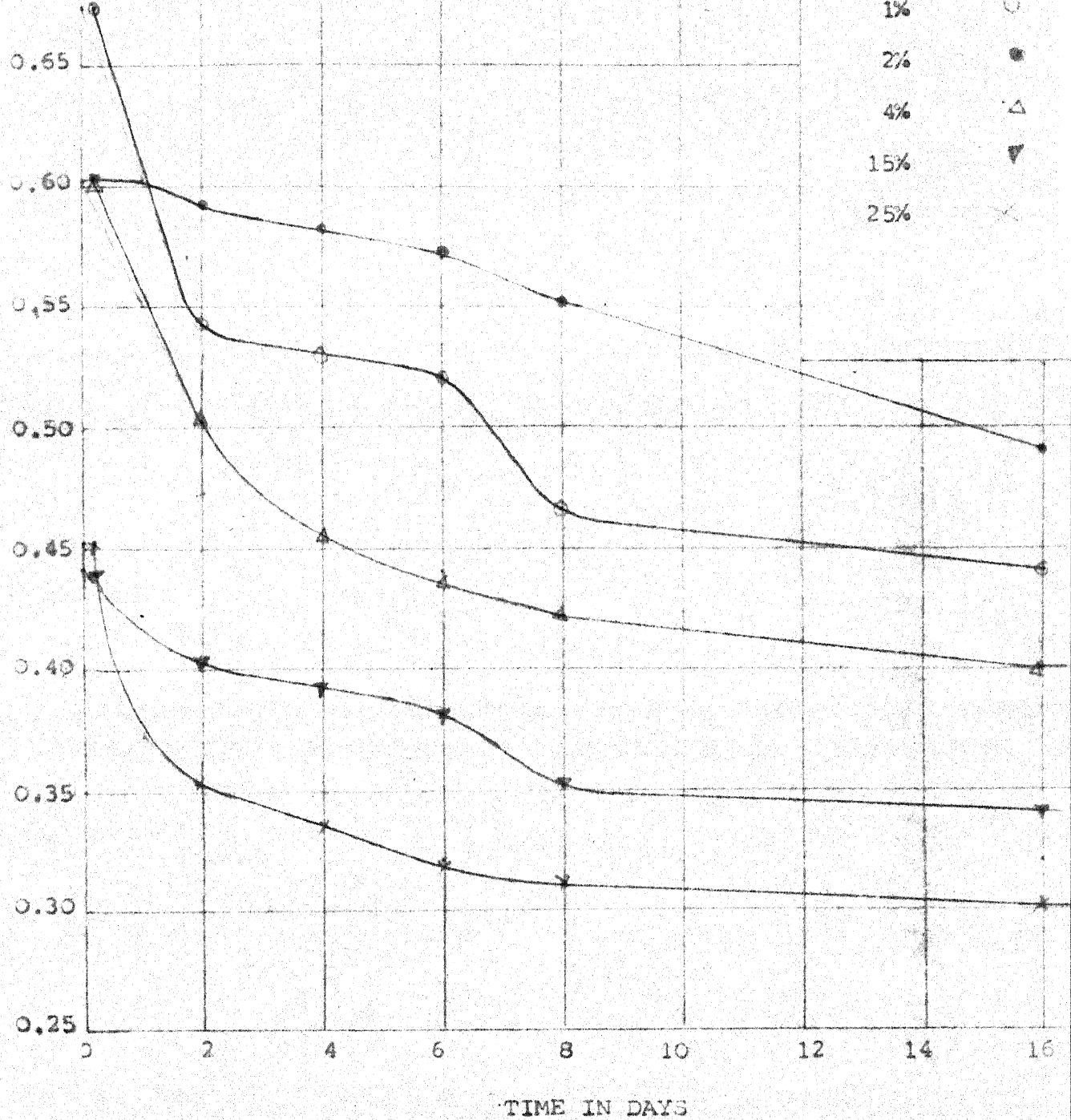


FIG. 14 CHANGE IN INTENSITY OF SiO_2 LINE OF BENTONITE ON AGING
LIME SAMPLES AT VARIOUS LIME LEVELS

In both the kaolinite - lime and bentonite - lime systems the silica has participated in its reaction with lime which has added to the growth of new minerals. In bentonite - lime systems however, an active role of silica is seen at all the percentages of lime with increasing periods of aging while in kaolinite - lime system beyond 8 days consumption of silica also seemed to have attained stability in its reaction participation.

(4) Growth of new products: The growth of new products appears to be somewhat related to several factors for example the hydration mechanism of the starting clay minerals, the extent to which the lime attacks the clay minerals, the CaO/SiO_2 ratio that is available in reaction stages and the nature of the cations present in the clay. Tobermorites form as products in most reactions in which calcium-ions and silicate-ions are brought together in aqueous solution. It comprises a range of calcium silicate hydrates which vary widely in both composition and degree of crystallinity. The reaction product which appears due to interaction of clay and lime is calcium silicate hydrate (1). It has a Ca/Si ratio less than 1.5. The hydration mechanism makes available the water of hydration that is necessary for the formation of the proper hydrated calcium aluminate silicates. In kaolinite - lime system, the characteristic formation and the rapid growth of the

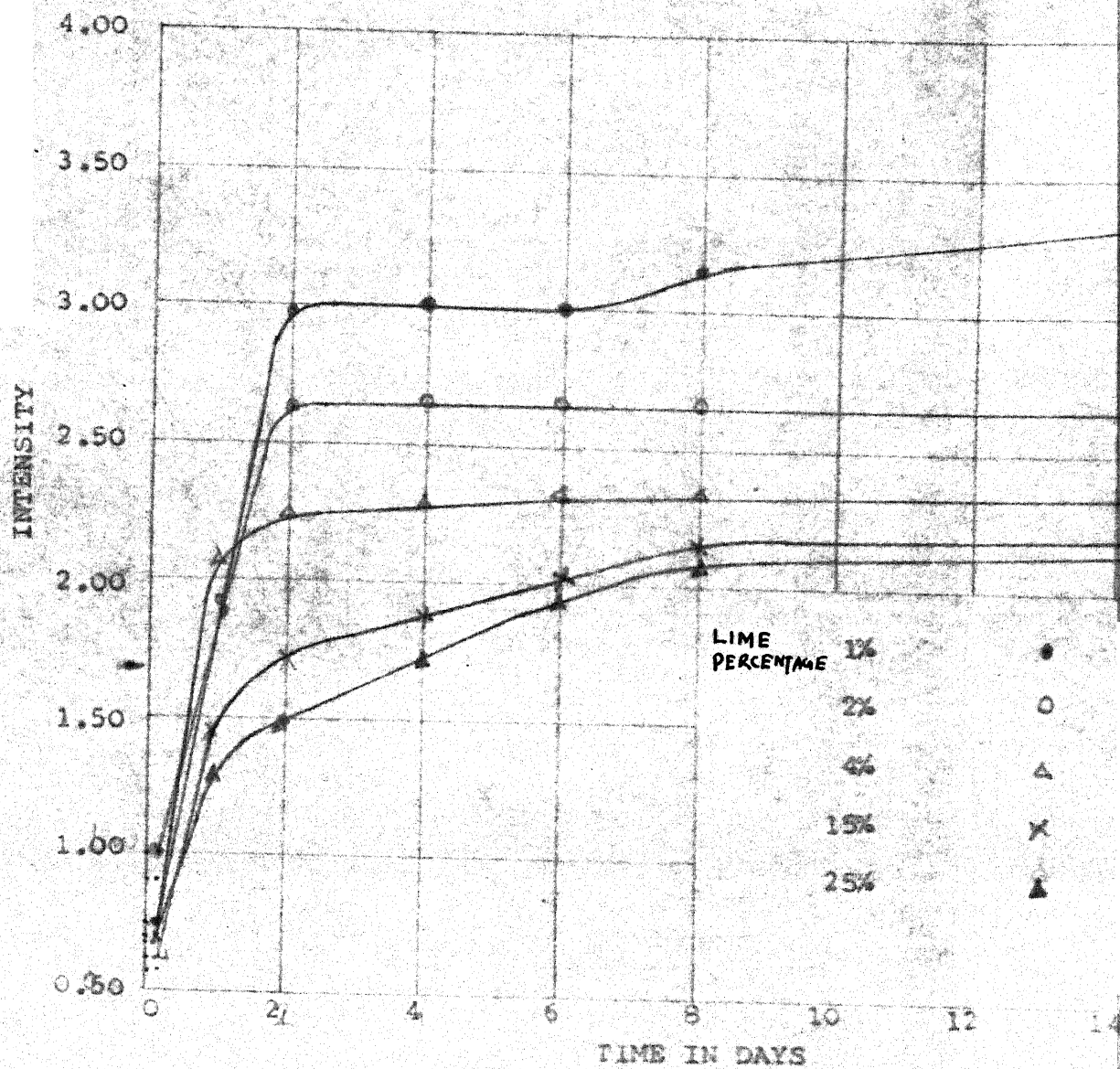


FIG. 15 CHANGE IN THE INTENSITY OF 20% LIME OF BENTONITE WITH THE NEW PRODUCT

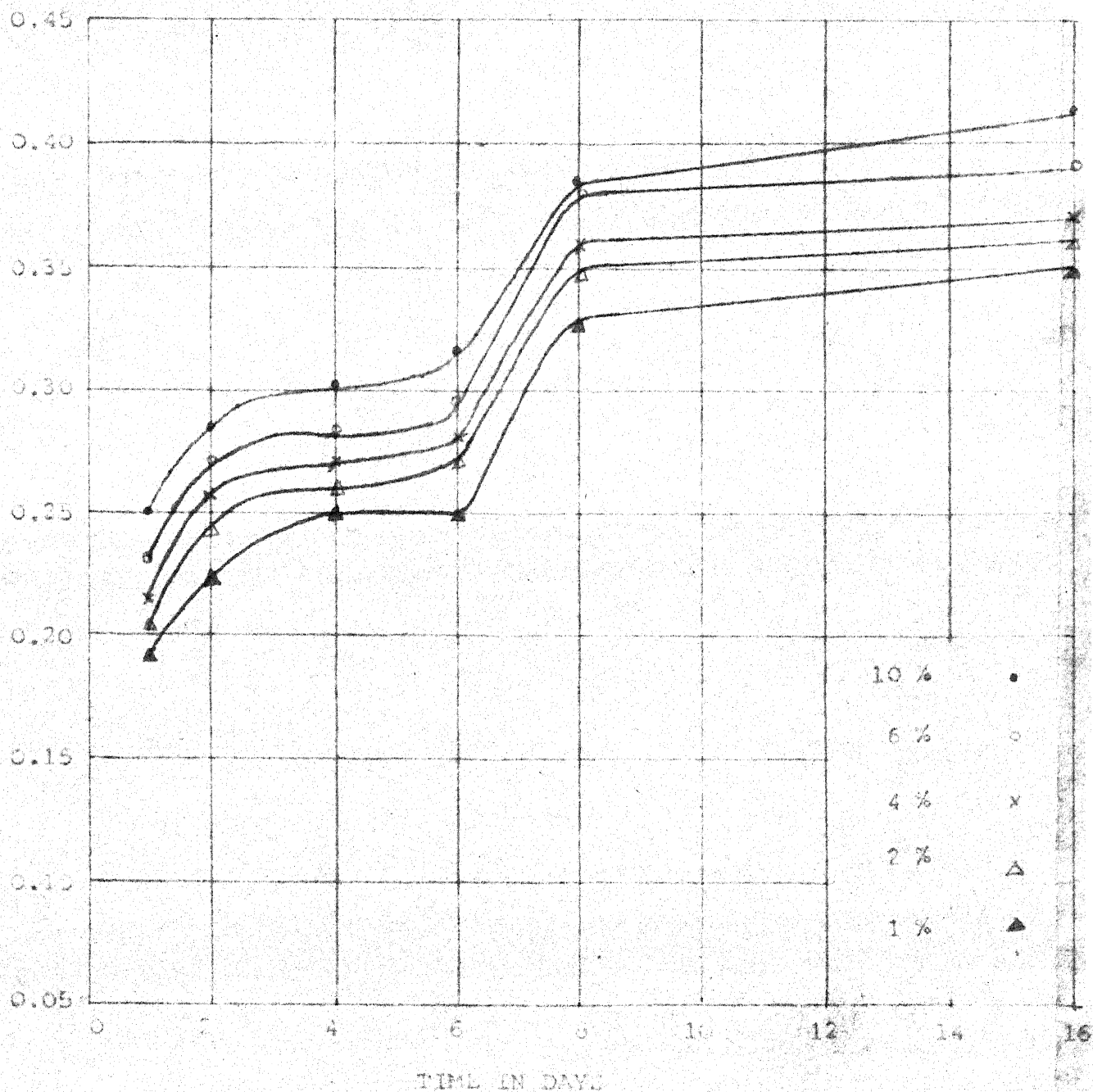


FIG. 18 INTENSITY CHANGES FOR 19.30° (2) LINE OF CELULITE DEVELOPED IN KAOLINITE-LIME SYSTEM ON AGING AT VARIOUS LIME LEVEL

prehnite (with the strong line at 4.60 \AA) might possibly be due to some of these variables which account for its absence in bentonite - lime system.

The various new compounds that are formed in both kaolinite - lime systems and bentonite - lime systems are represented in tables 2 and 3 and figures 19, 21, 23, 25, 27, 29, to 33. As explained certain lines for these new products have overlapped the lines for other materials involved in the reaction and as such have created difficulties for listing all the lines.

In kaolinite - lime systems an immediate attack with lime on kaolinite is responsible for the formation of prehnite. The limited adsorption of Ca-ions on to the surface of clay is evident from the absence of the characteristic broadening that is noticed in case of montmorillonite lines of the bentonite - lime system. Sloane (1964) has identified the instantaneous development of prehnite in short term reactions in kaolinite - lime systems and confirmed the presence of ^{the} same from electron diffraction data too. Eades and Grim (1960) do not report this compound in longer - term reactions of kaolinite - lime systems. Thus the results from the present investigation confirm the thinking that prehnite may be a reaction product of ephemeral phase.

Formation of hydrogarnets as also the other compounds stated in these systems has also been observed

TABLE 2

X-RAY DIFFRACTION DATA FOR SEPARATE LINES
OF NEW PRODUCTS IN KAOLINITE-LIME
SYSTEMS WITH CuK_α RADIATION*

2	λ d λ (in \AA°)	λ Tentatively identified new mineral λ	λ Source of data for identifica- tion.
11.80 -11.20	7.49 -7.89	Tetra Calcium aluminate hydrate.	Croft (1964)
14.40 -14.20	6.14 -6.23	Unidentified	-
17.40 -17.20	5.09 -5.15	Hydrogarnets	Croft (1964)
19.40 -19.20	4.57 -4.61		
25.58	3.48	Prehnite	Sloane (1964)
2.54 - 2.56	35.20 -34.90		

*This table does not include the other lines for all the products stated since they overlap the lines for either the clay or lime used.

TABLE 3

X-RAY DIFFRACTION DATA FOR SEPARATE LINES
OF NEW PRODUCTS IN BENTONITE-LIME
SYSTEMS WITH CuK RADIATION*

2	d (in \AA)	Tentatively identified new mineral	Source of data for identifica- tion.
11.60 -11.18	7.62 -7.90	Ill-crystallized tobermorite	Croft (1964)
29.18 -28.80	3.05 -3.09	Crystallized calcium silicate hydrate (1)	Croft (1964)
14	6.32	Unidentified	-
20°	4.43	Unidentified	-
31.30 -30.70	2.85 -2.90	Tetra calcium aluminate hydrate	Croft (1964)

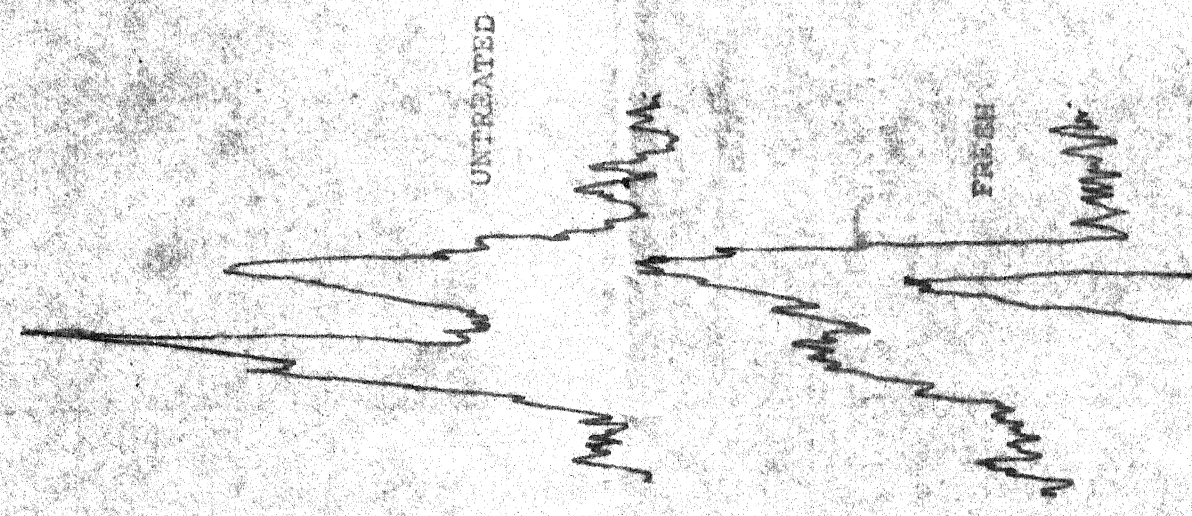
*This table does not include the other lines for all the products stated since they overlap the lines for either the clay or lime used.

by Croft (1964). However no effort has been made for a detailed quantitative estimation of the rate of involvement of the constituents and the effect of aging.

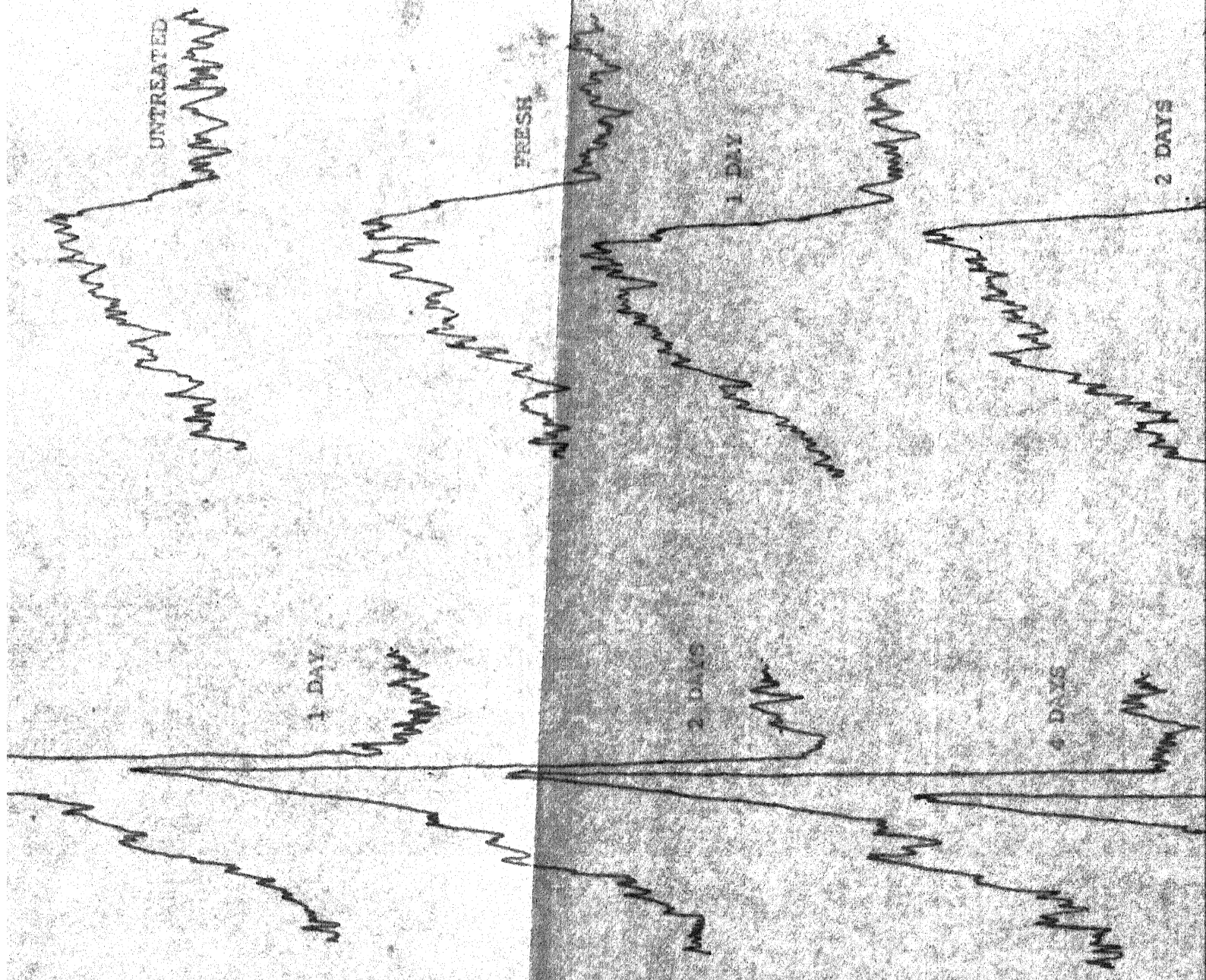
In bentonite - lime systems the conspicuous compounds that involve the initial consumption of montmorillonite appears to be the formation of a hydrated calcium silicate with lines at 4.43 \AA° and 6.32 \AA° . Identification of the compound could not be done due to the overlapping of the peak at 4.43 \AA° with the montmorillonite peak at 4.26 \AA° (Figures 19, 21, 23, 25 and 27). The formation of the compound tetracalcium aluminate hydrate (C_4AH_{13}) is seen in both kaolinite and bentonite systems with lime. Such an observation is in confirmity with Croft (1964). However an additional compound with the composition calcium silicate hydrate has been identified in bentonite which is not seen in kaolinite - lime systems.

Thus the X-ray diffraction data have indicated the extent of participation of the different constituents - kaolinite, montmorillonite, free silica, excess lime and the various reaction products that are present at any stage in the process of clay - lime stabilization. In addition the reaction products except for C_4AH_{13} have been found to be different for both the systems. While hydrogarnets and prehnite dominate in kaolinite - lime systems, ill-crystallized tobermorite and CSH(1) are present in the bentonite - lime systems.

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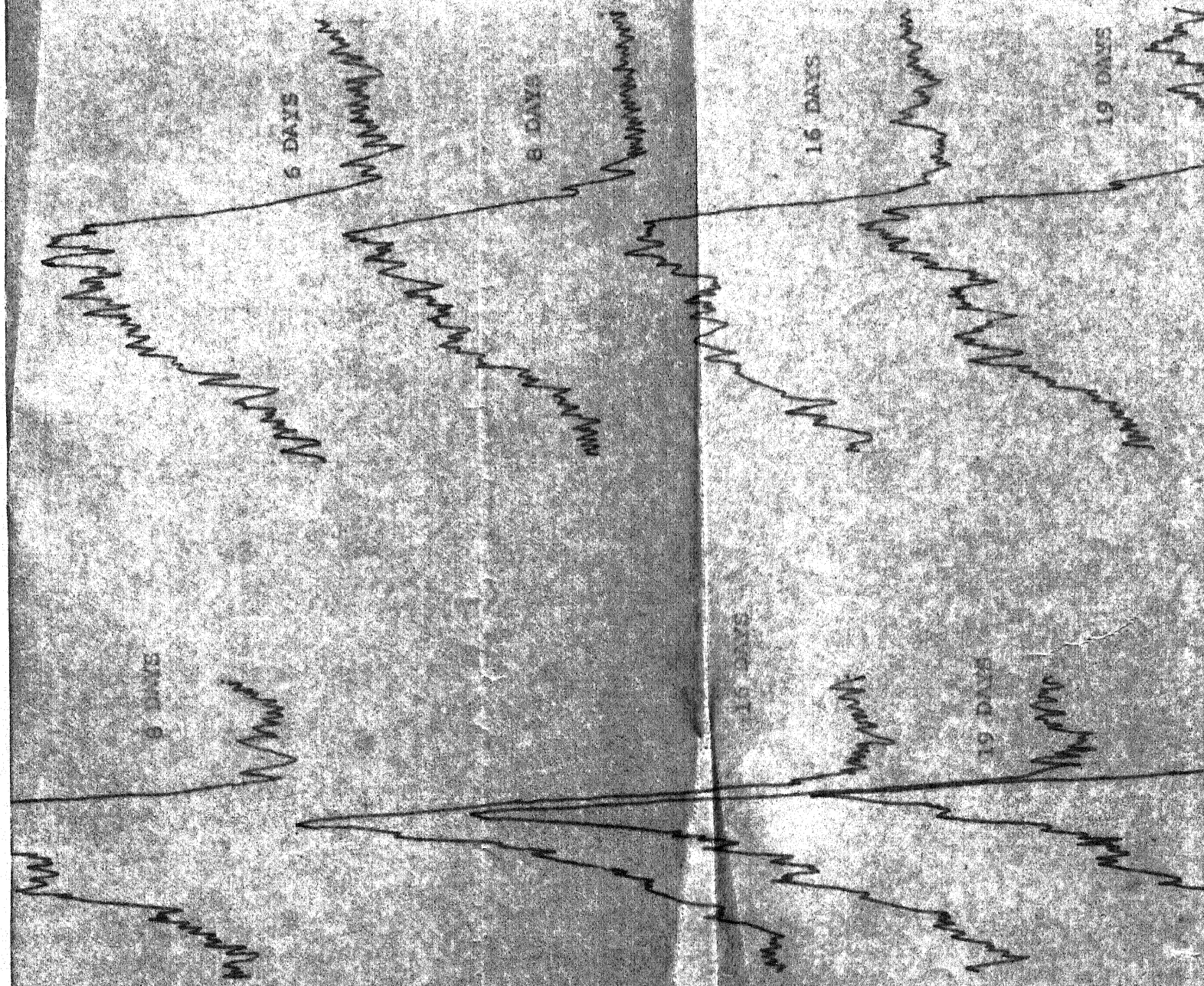


FIG. 19 X-RAY DIFFRACTION PATTERNS OF BENTONITE-LIME SYSTEM WITH 2% LIME ON AGING TO DIFFERENT TIME PERIODS. GROWTH OF NEW PRODUCT IS INDICATED BY DEVELOPMENT OF 20° (2θ) PEAK.

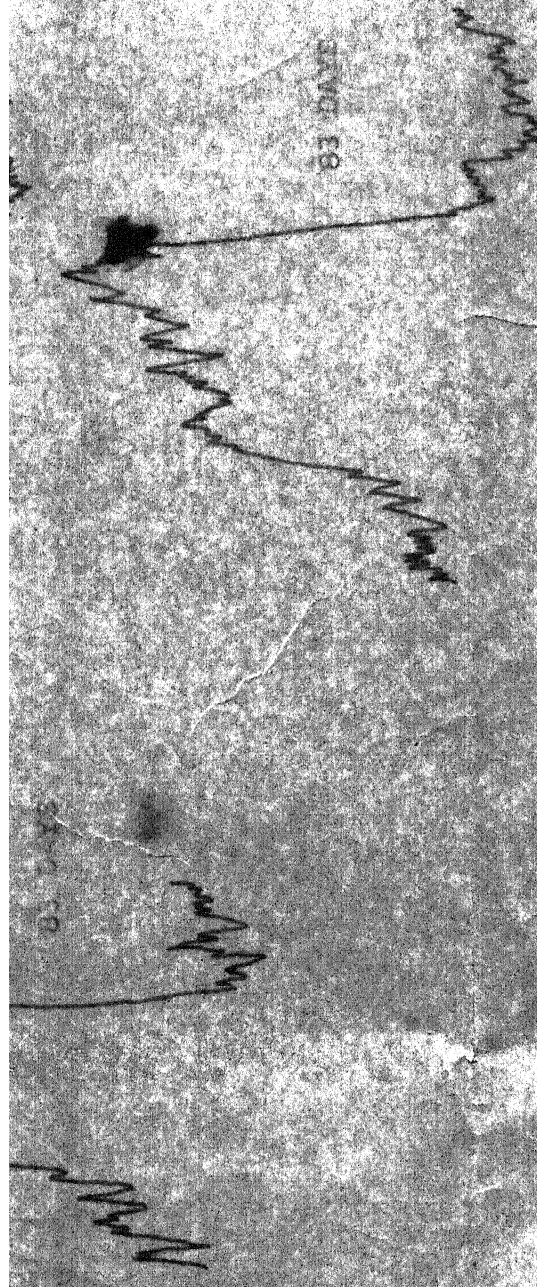
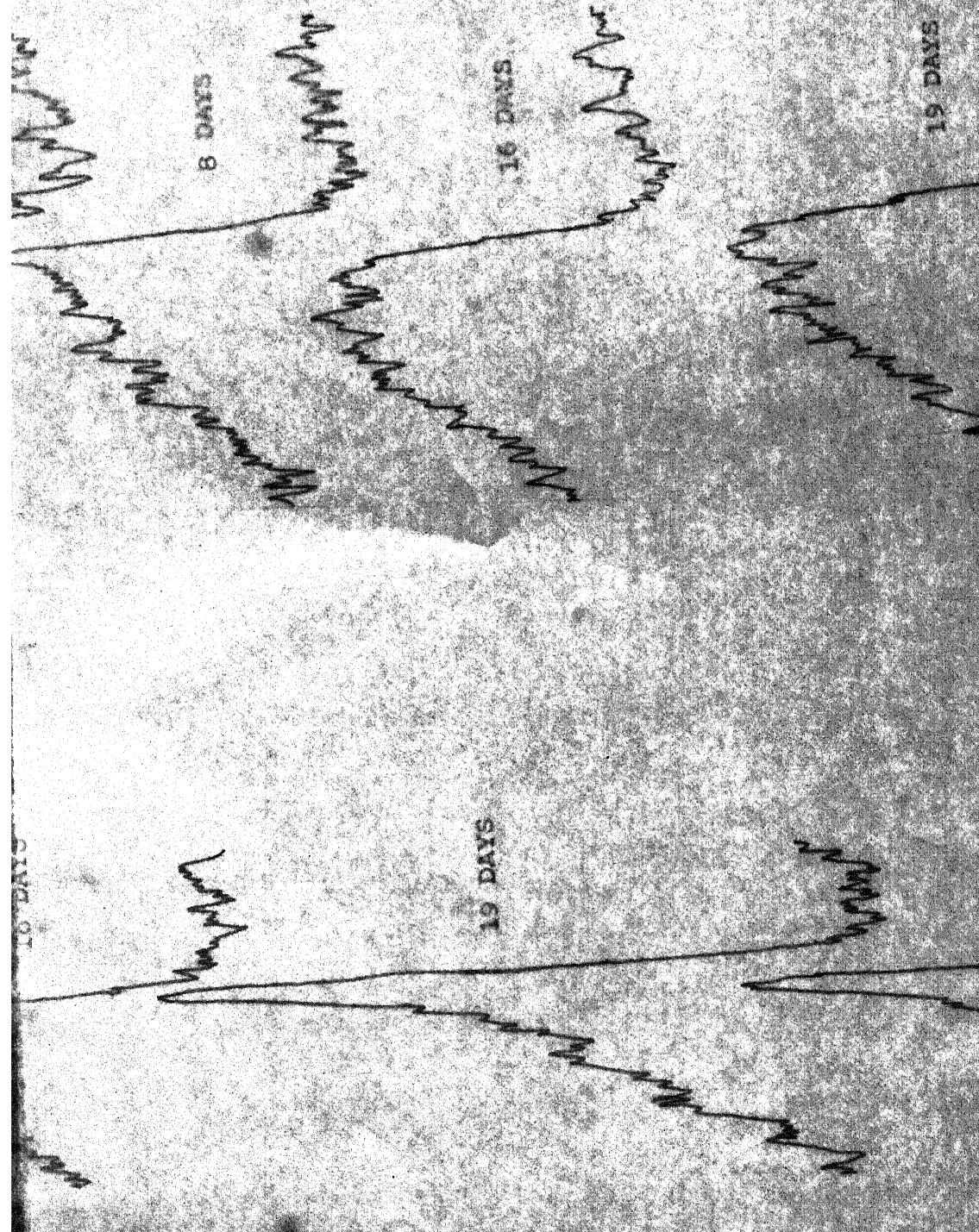


FIG. 20 X-RAY DIFFRACTION PATTERNS OF BENTONITE-LIME SYSTEM WITH 2% LIME ON AGING TO DIFFERENT TIME PERIODS. GROWTH OF NEW PRODUCT IS INDICATED BY DEVELOPMENT OF 20° (2θ) PEAK.



23 X-RAY DIFFRACTION PATTERNS OF BENTONITE-LIME SYSTEM WITH LIME AGING TO DIFFERENT TIME PERIOD. GROWTH OF NEW PRODUCT IS INDICATED BY DEVELOPMENT OF $20^\circ (2\theta)$ PEAK.

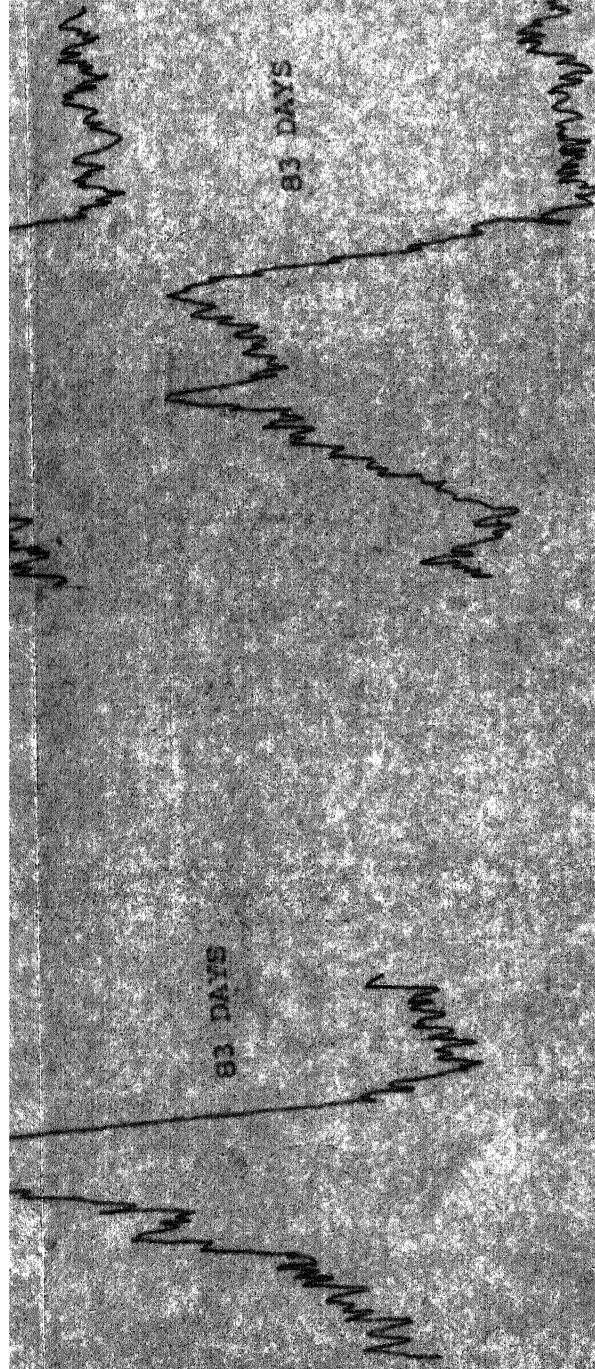
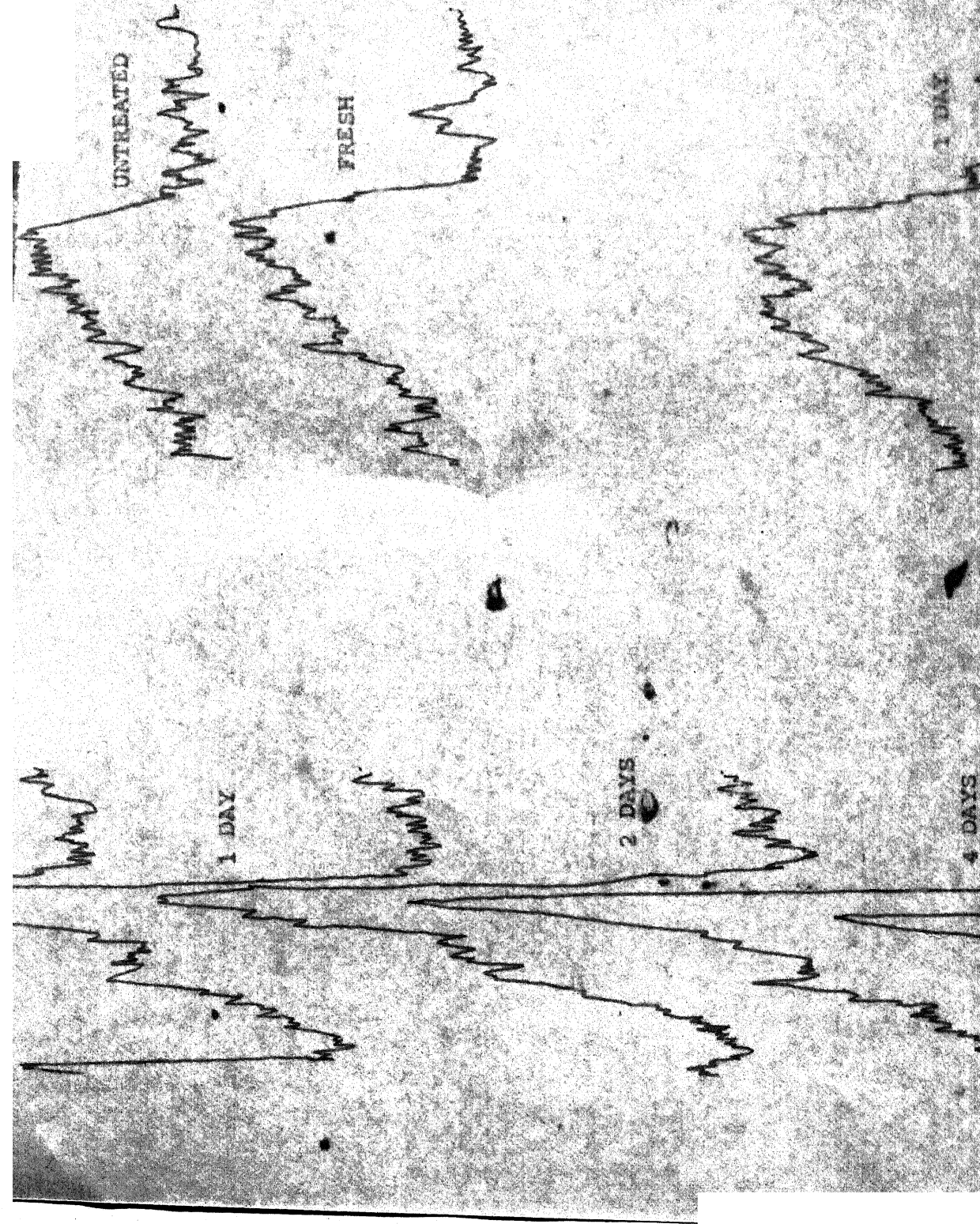
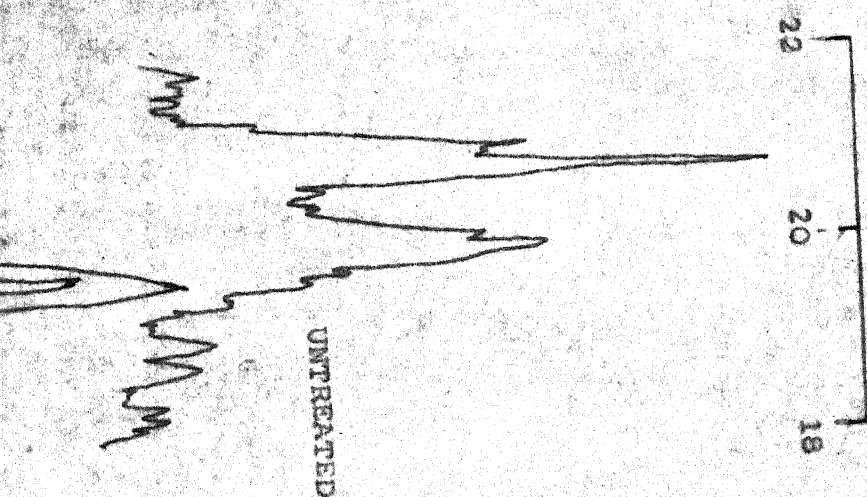


FIG. 24 X-RAY DIFFRACTION PATTERNS OF BENTONITE-LIME SYSTEM WITH LIME AGING TO DIFFERENT TIME PERIOD. BROADENING OF THE PEAK AT $35^\circ (2\theta)$ IS SHOWN.





20
30 28

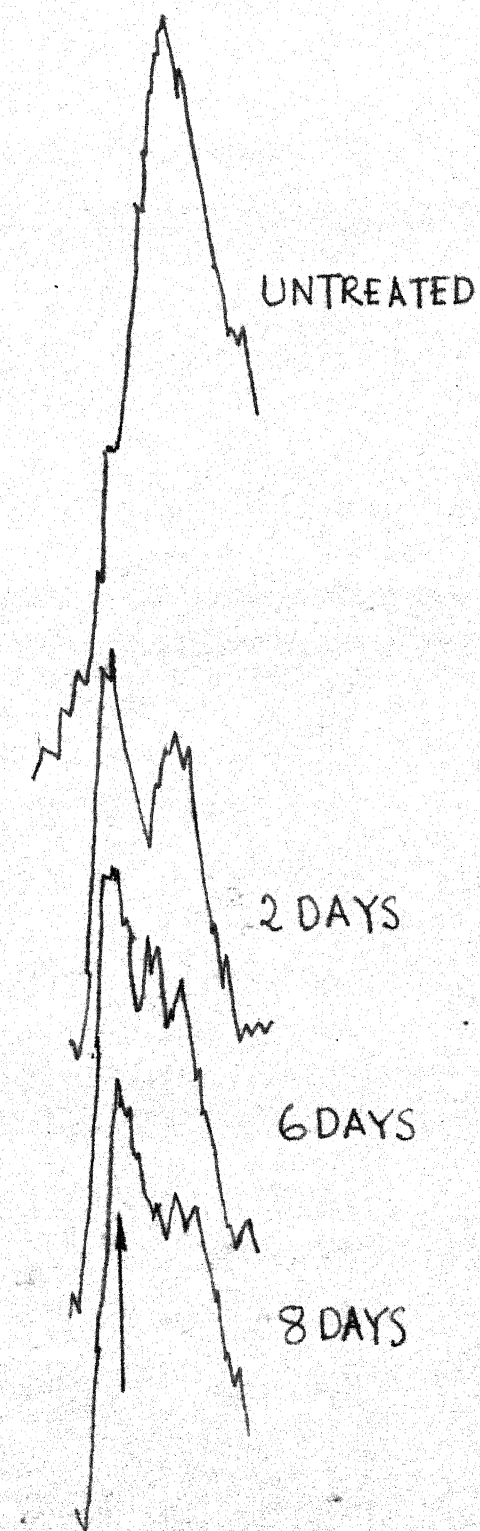


FIG. 29. X-RAY DIFFRACTION TRACES
FOR BENTONITE-LIME SAMPLE
WITH 15% LIME. ARROW INDICATES

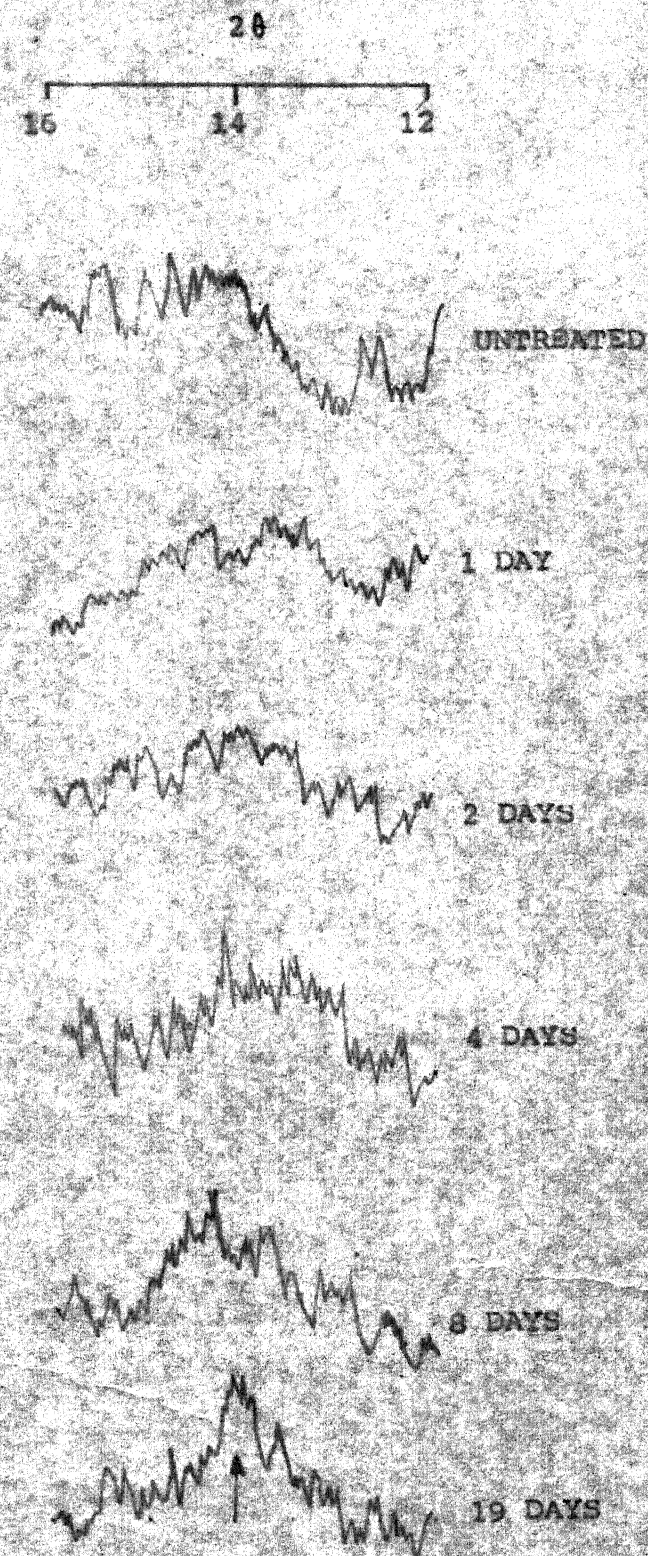
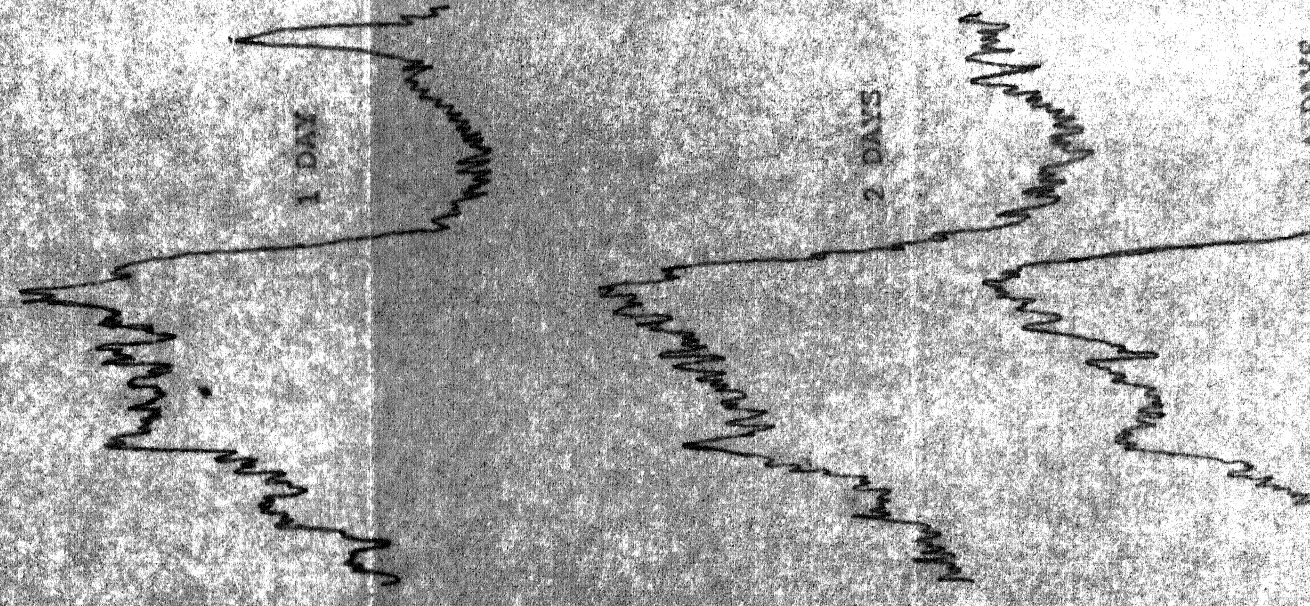
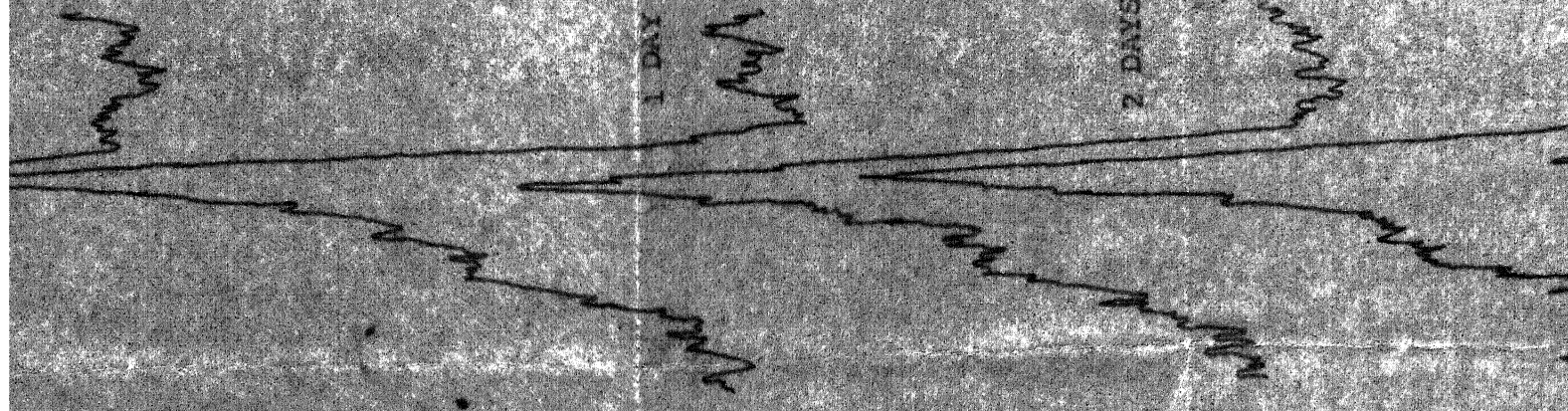
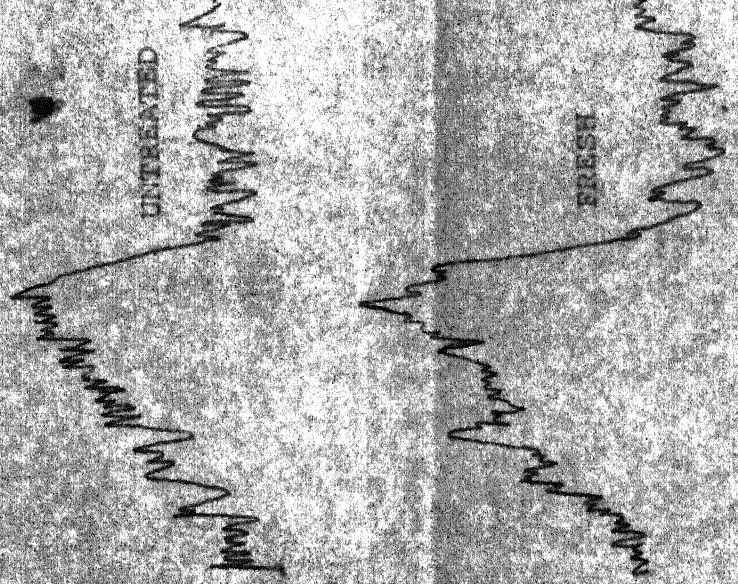
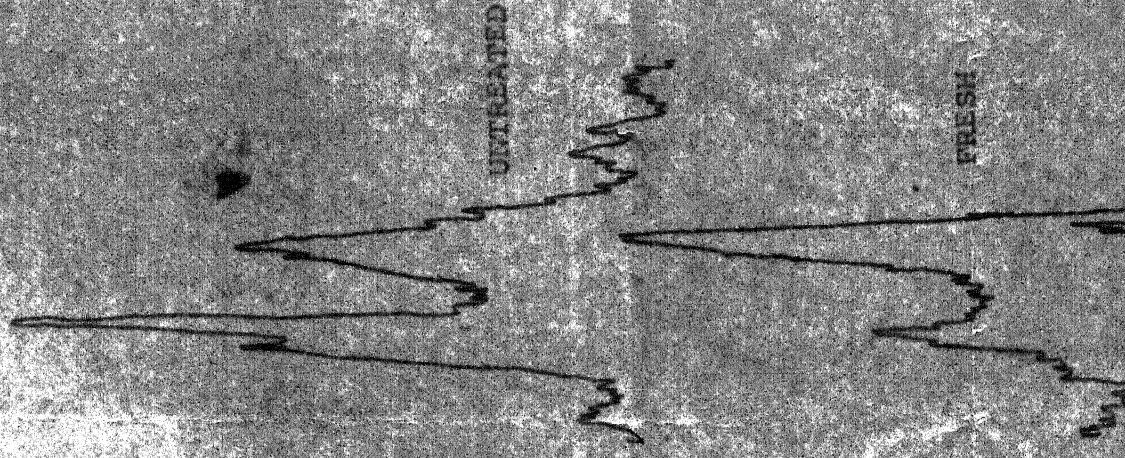


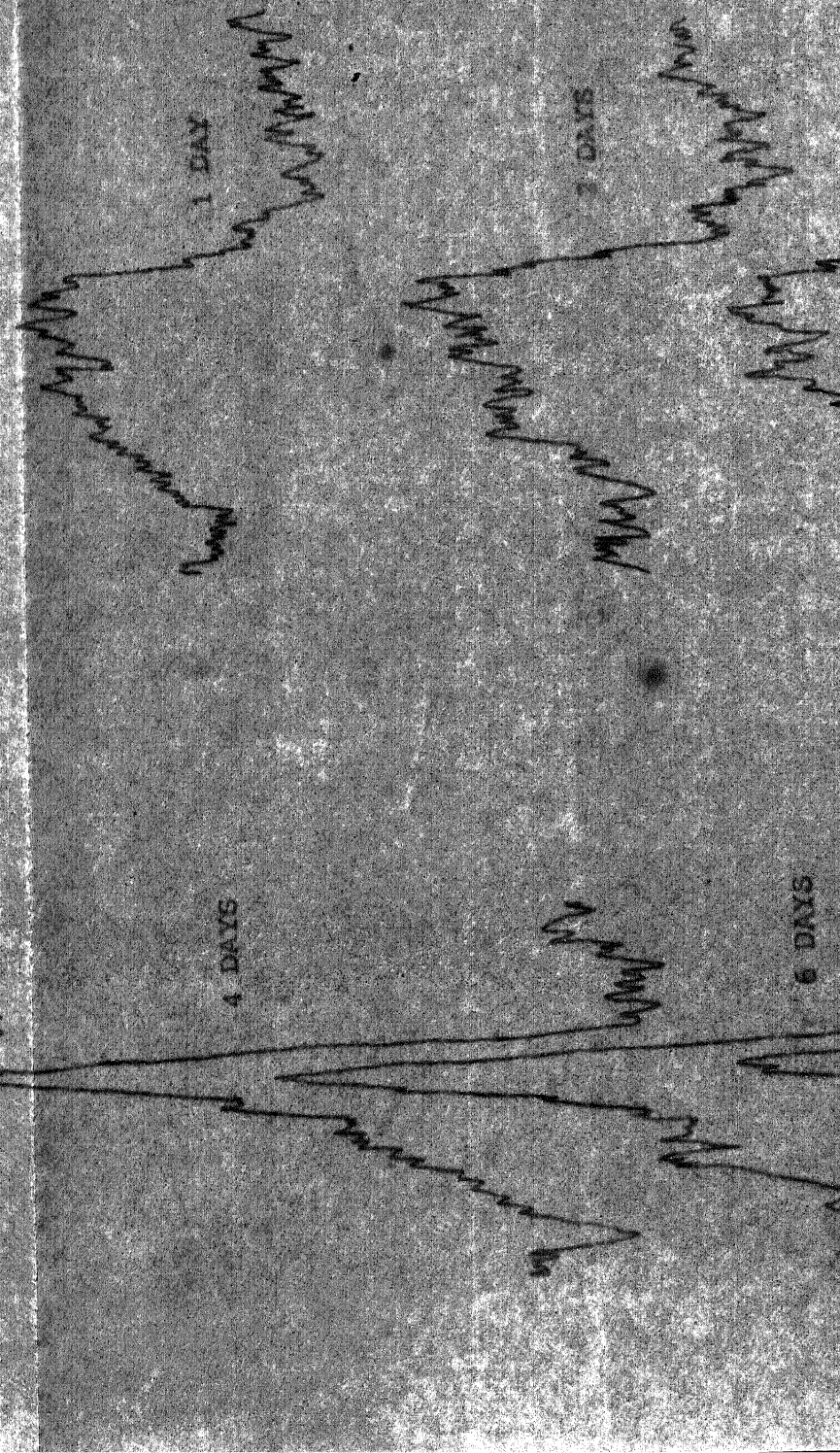
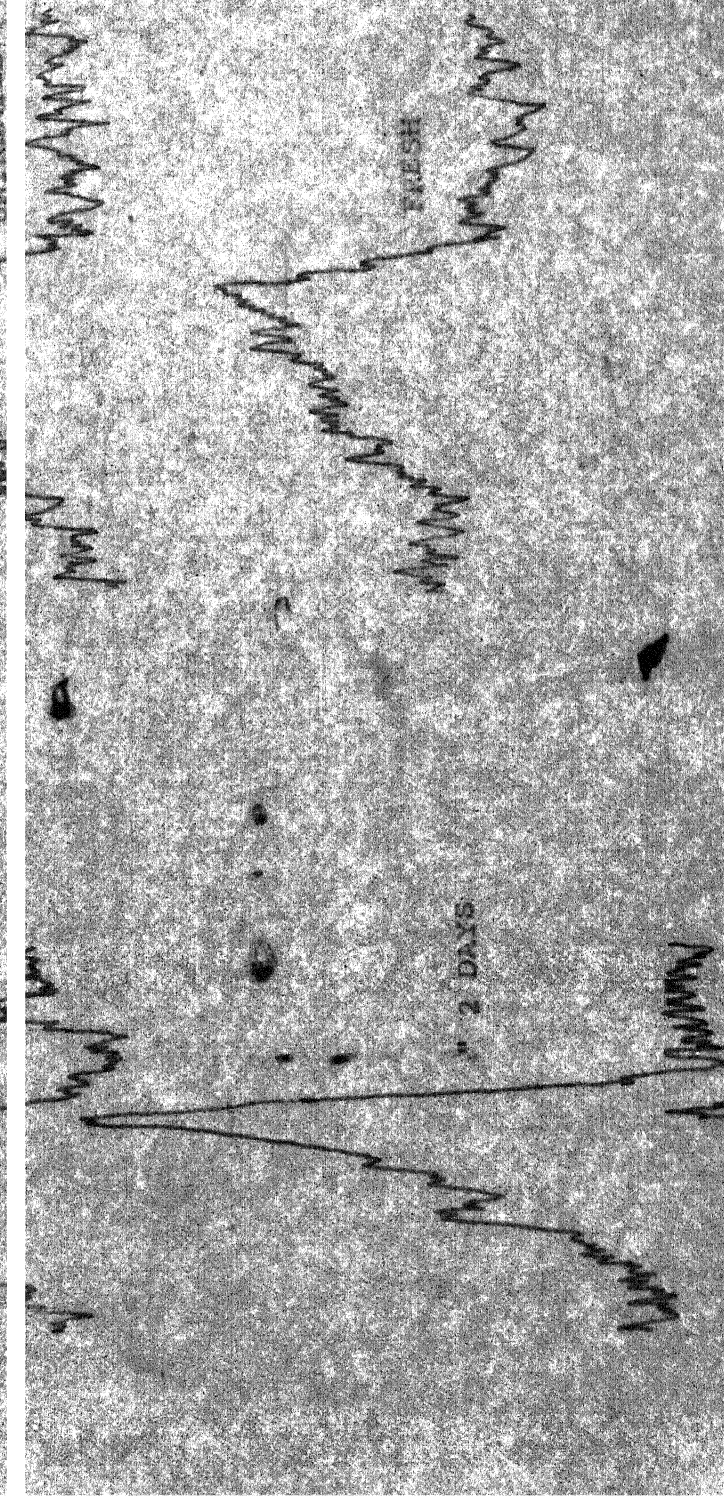
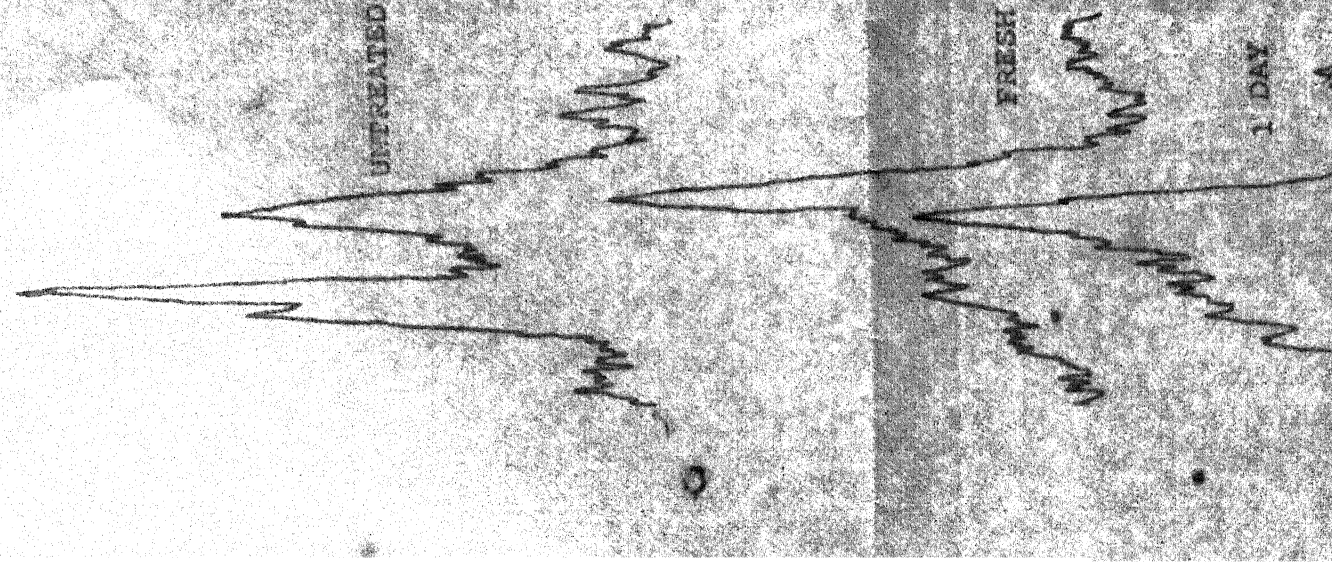
FIG. 30 X-RAY DIFFRACTION TRACES FOR BENTONITE-LIME SAMPLES WITH 4% LIME. ARROW INDICATES NEW PRODUCT (CaK_2 RADIATION).

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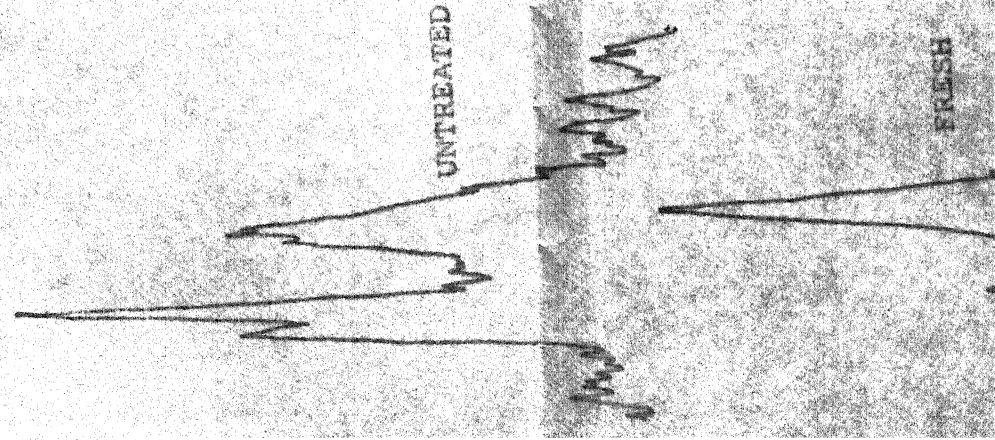
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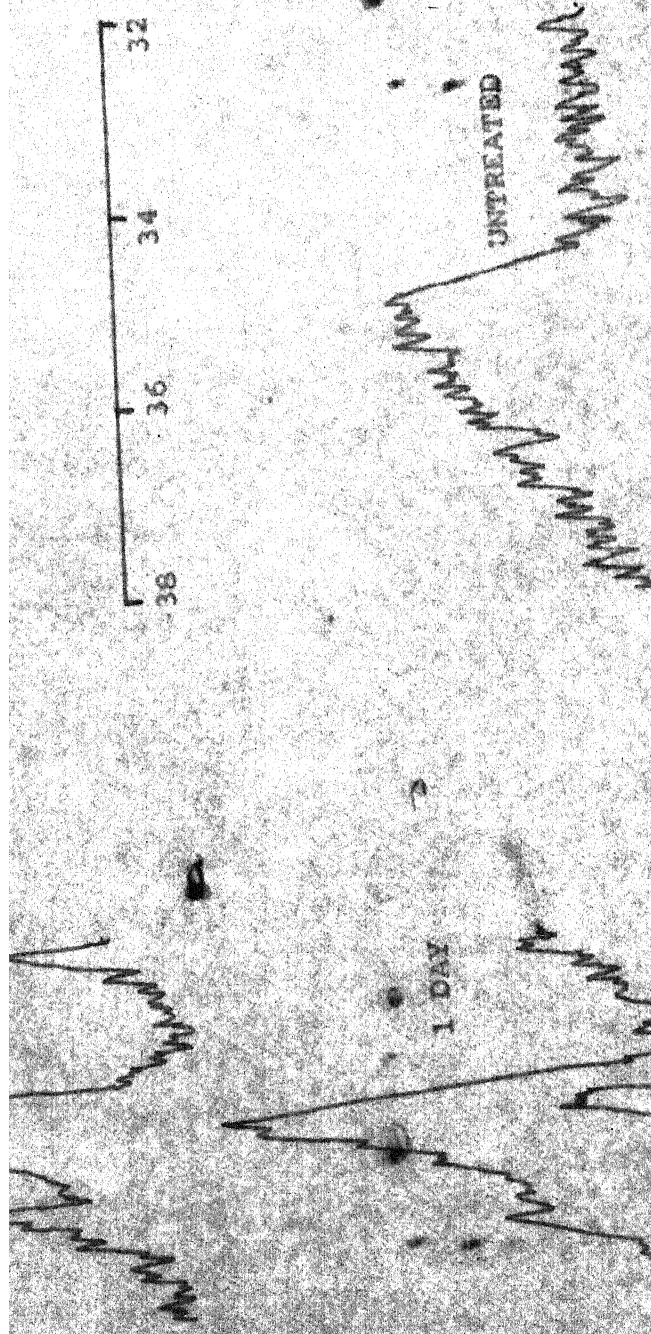
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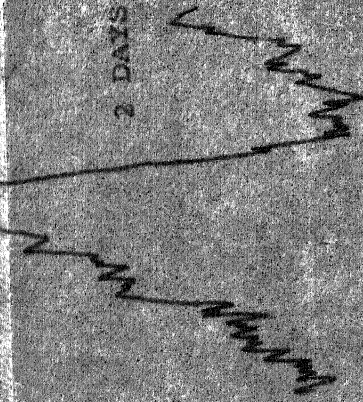
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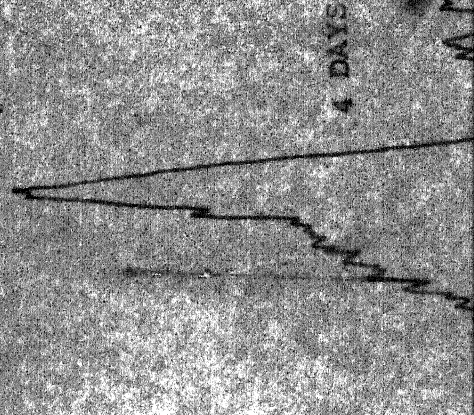
38 36 34 32



2 DAYS

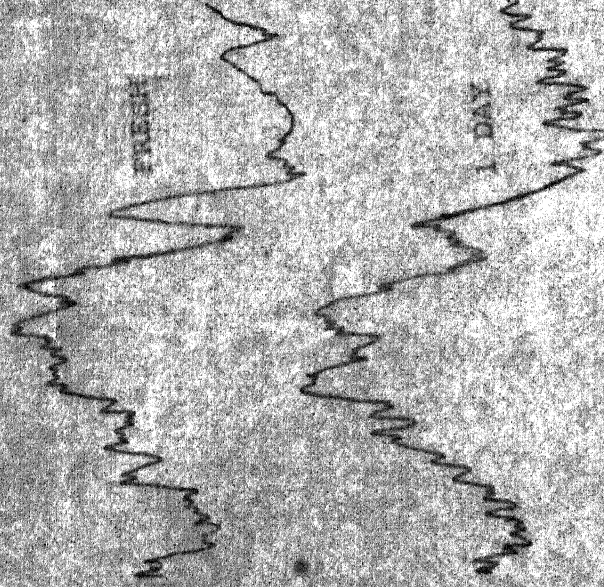


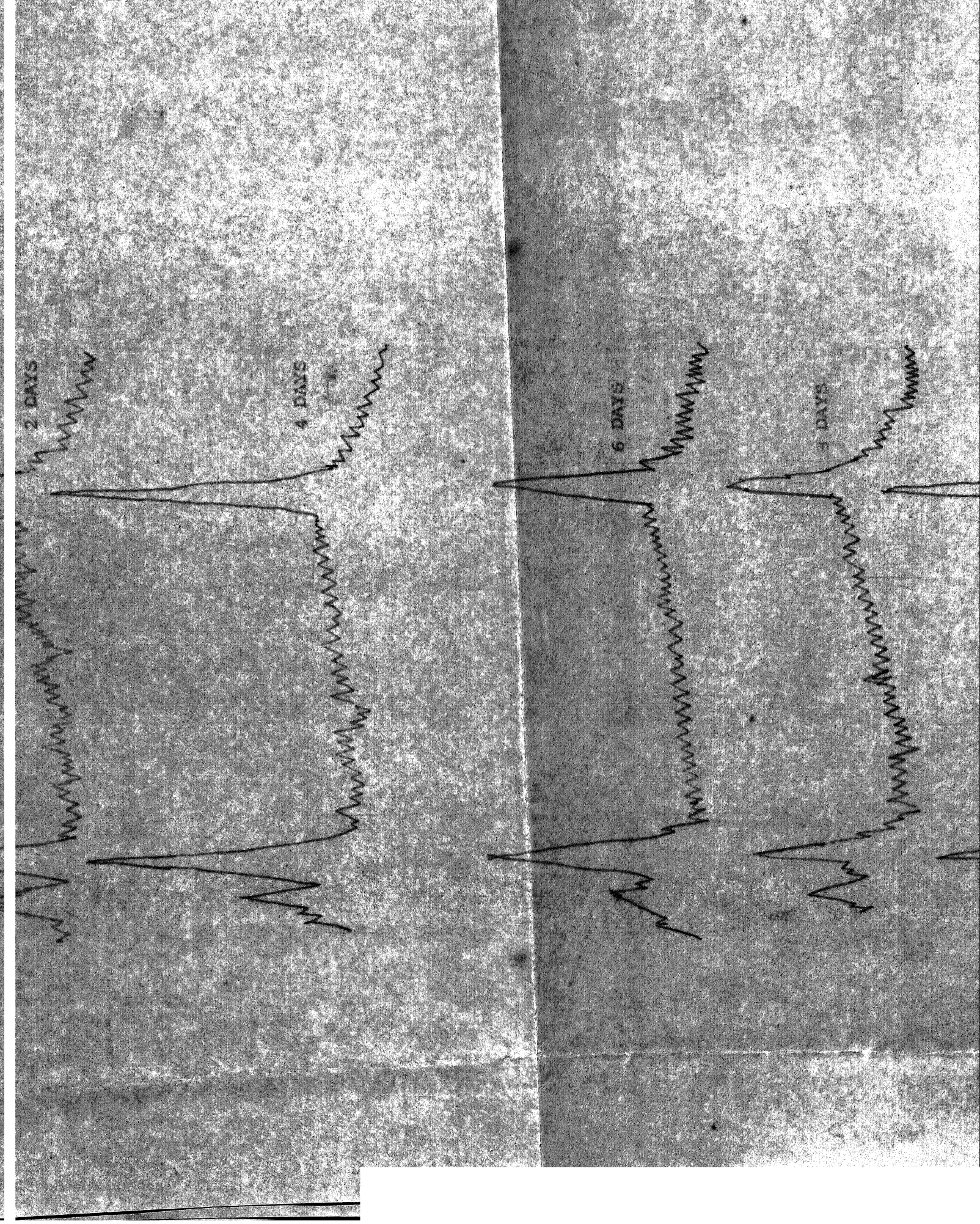
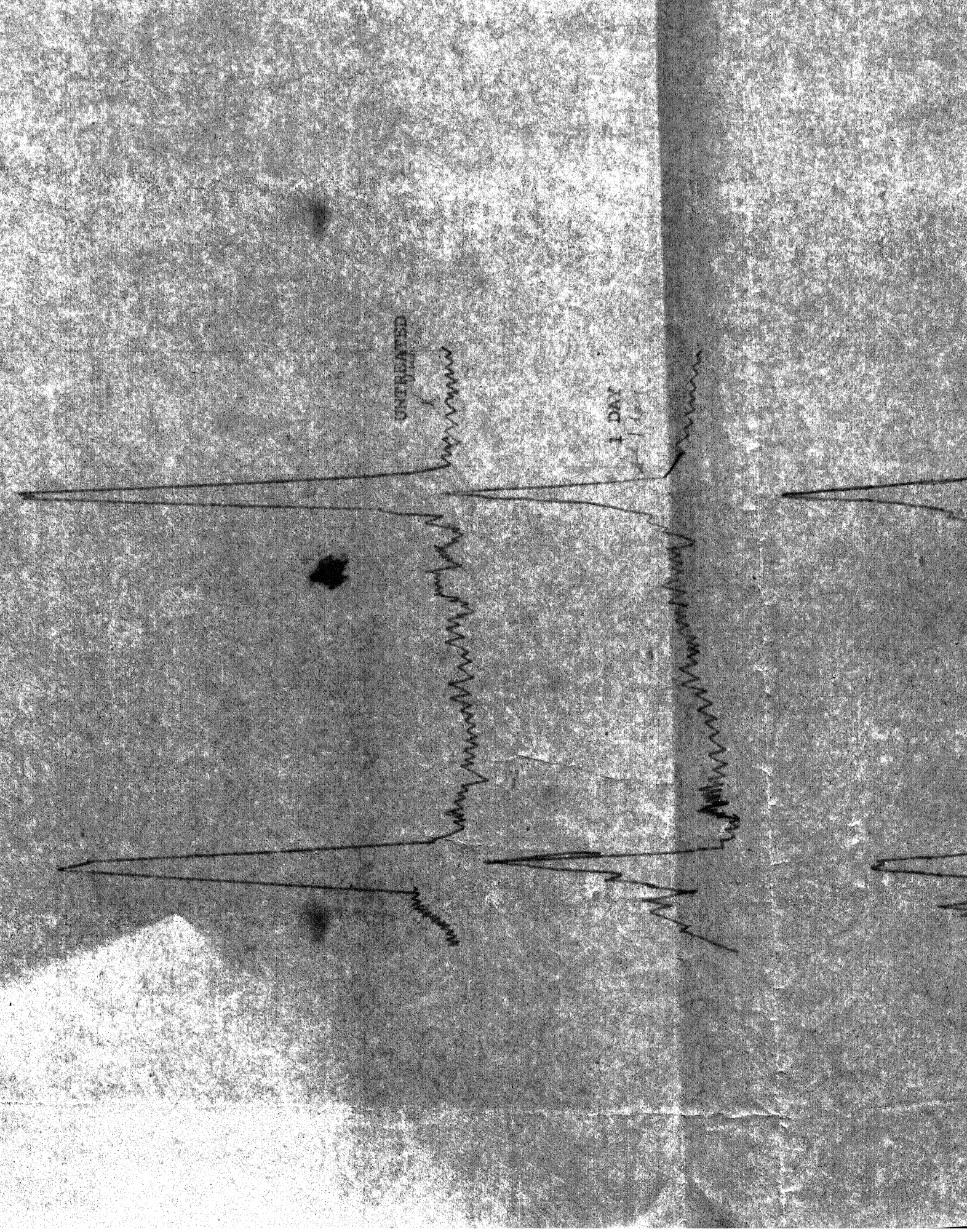
4 DAYS

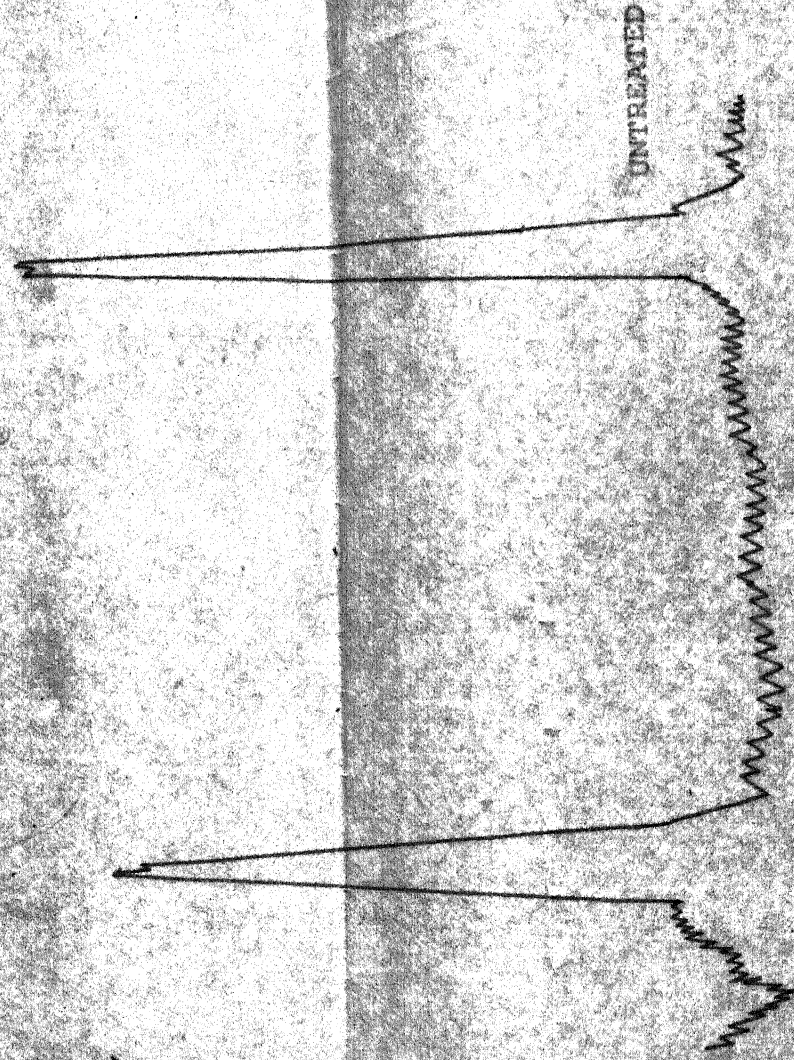


FRESH

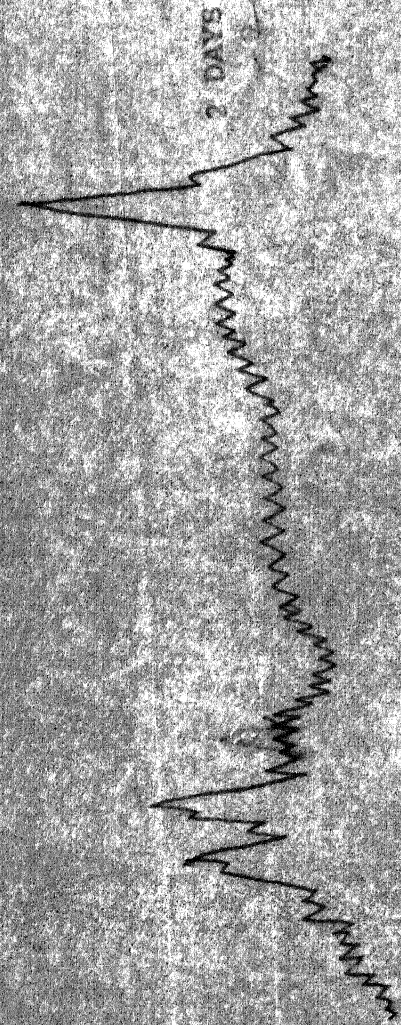
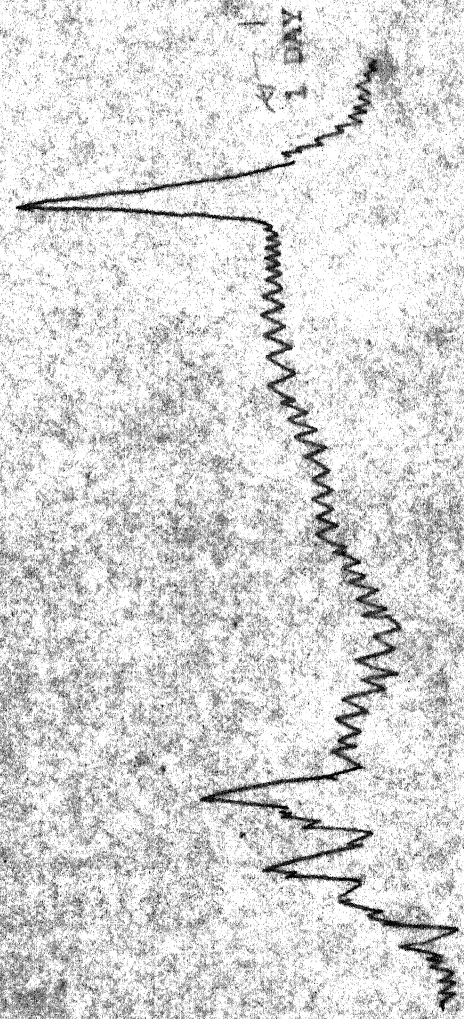
1 DAY

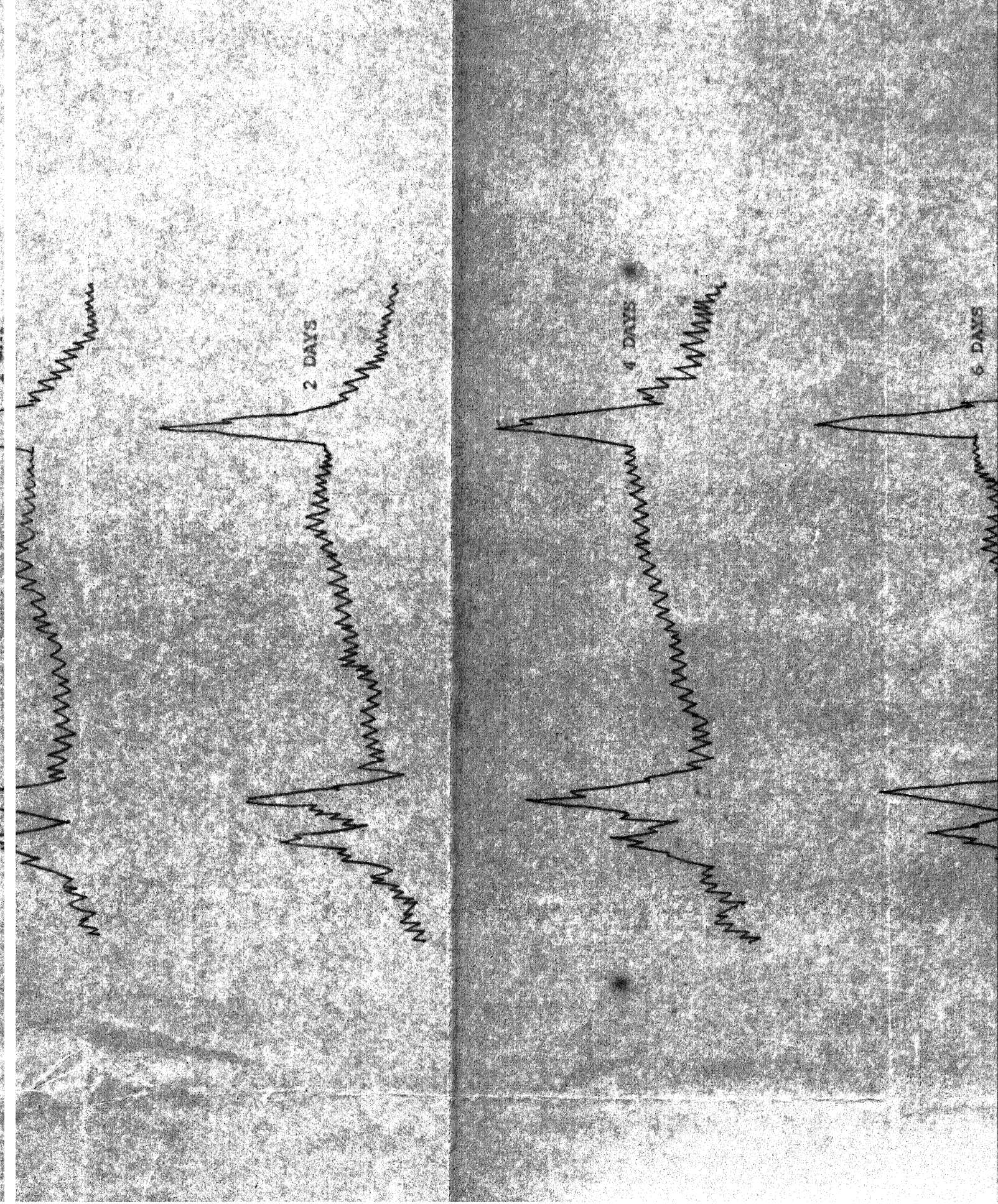
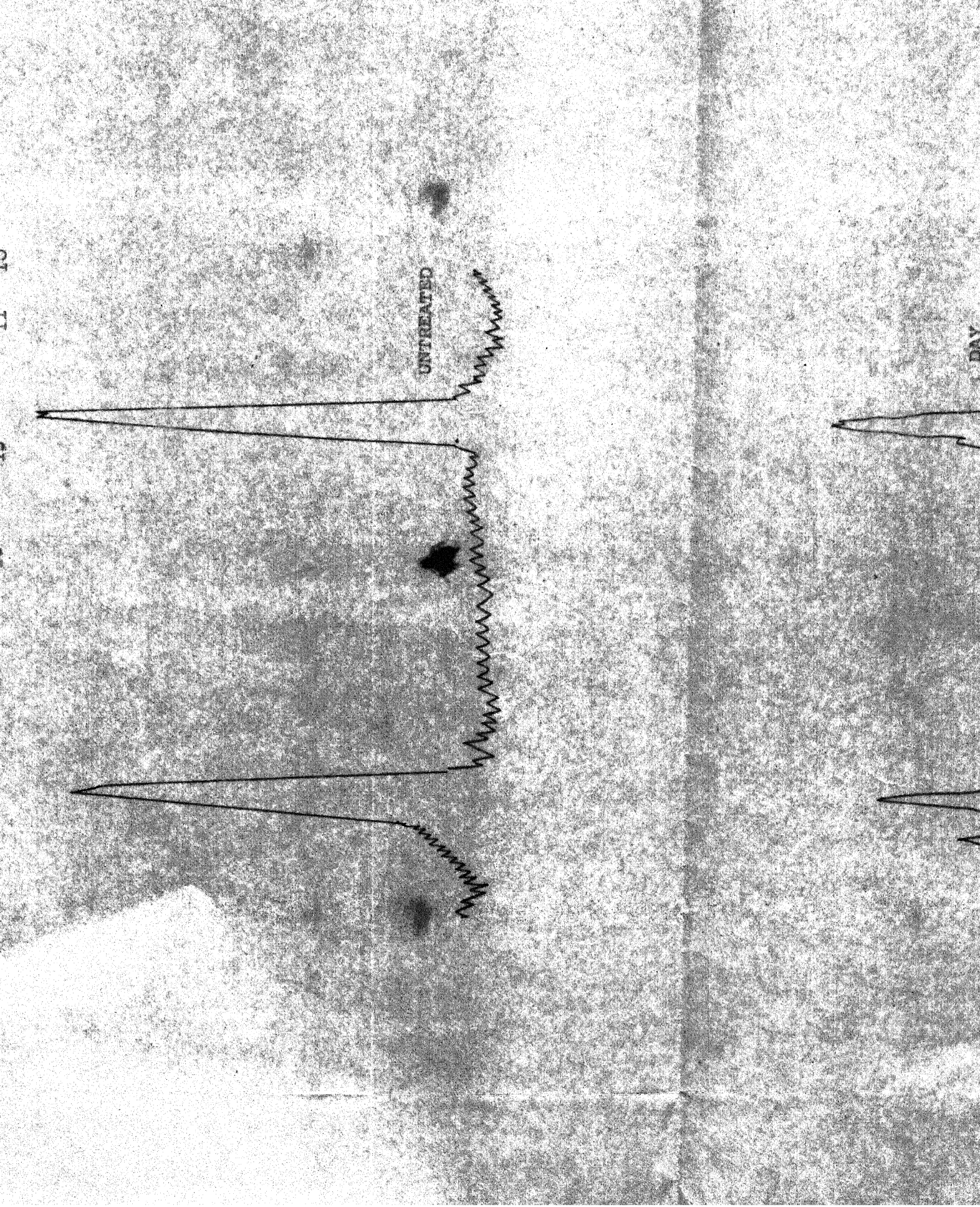






10%





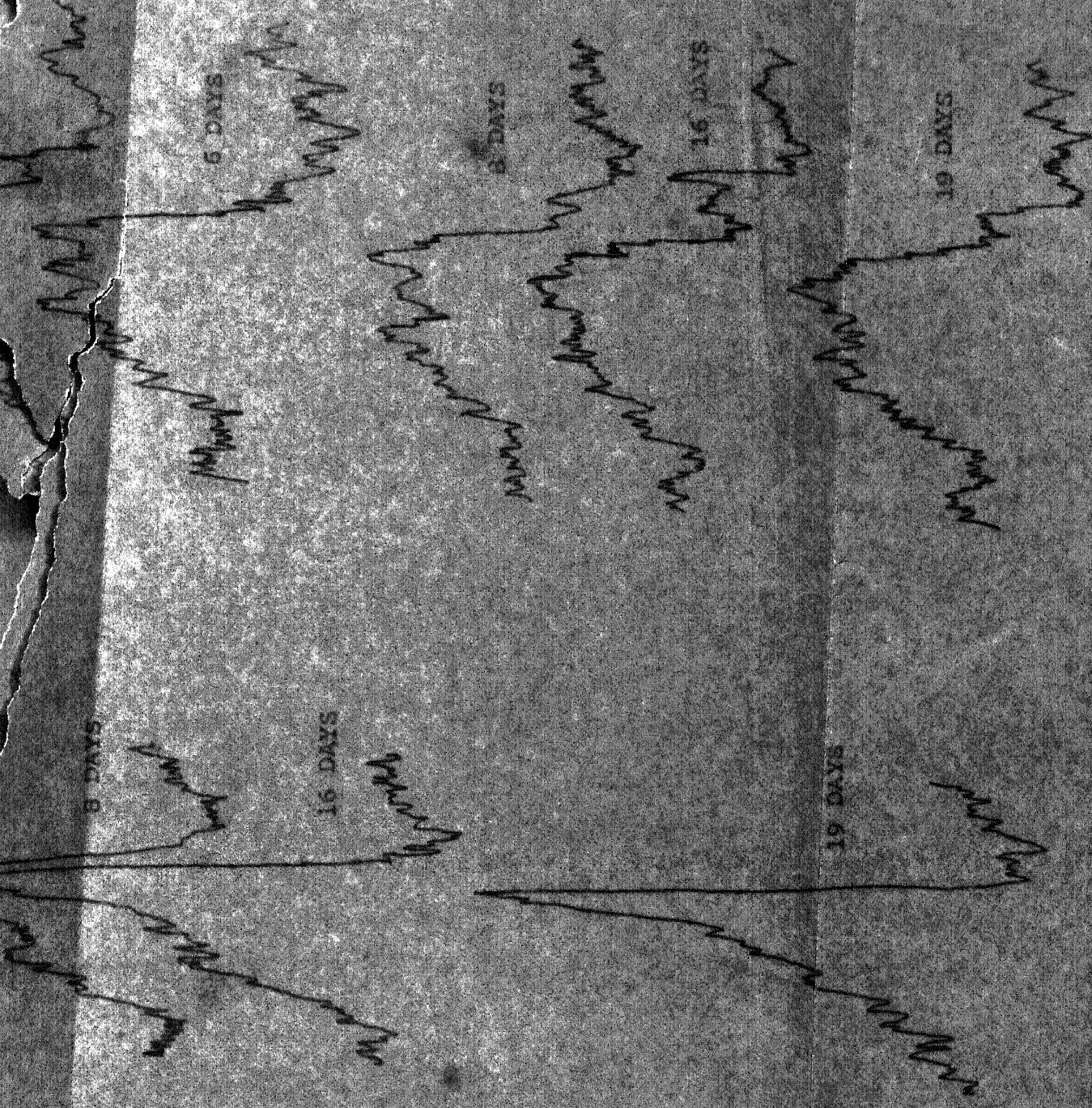


FIG. 25 X-RAY DIFFRACTION PATTERNS OF BENTONITE-LIME SYSTEM WITH 15% LIME ON AGING TO DIFFERENT TIME PERIOD. GROWTH OF NEW PRODUCT IS INDICATED BY DEVELOPMENT OF 200 (2θ) PEAK.

FIG. 26 X-RAY DIFFRACTION PATTERNS OF BENTONITE-LIME SYSTEM WITH 15% LIME ON AGING TO DIFFERENT TIME PERIOD. BROADENING OF THE PEAK AT 35° (2θ) IS SHOWN.

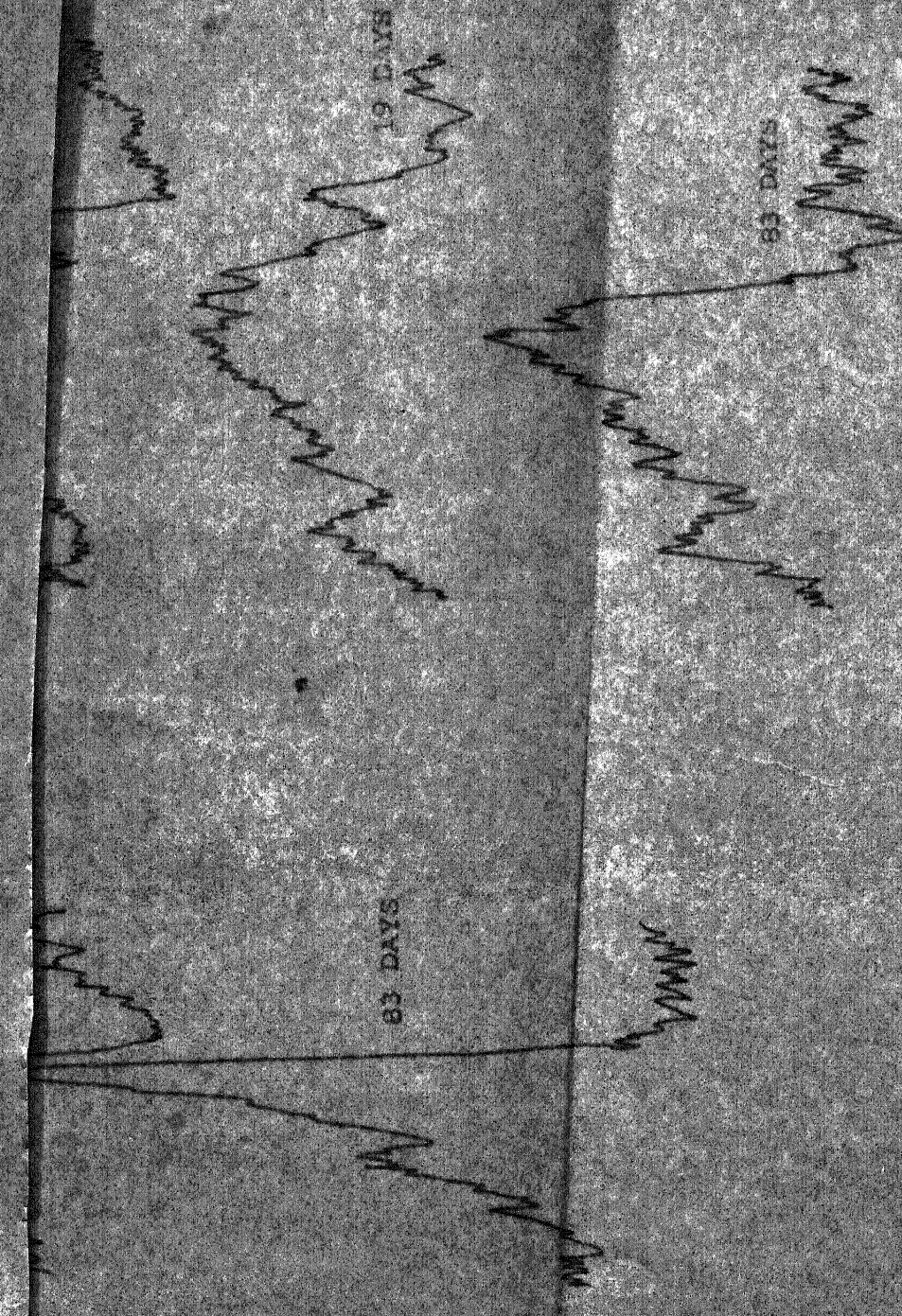


FIG. 27 X-RAY DIFFRACTION PATTERNS OF BENTONITE-LIME SYSTEM WITH 25% LIME ON AGING TO DIFFERENT TIME PERIOD. GROWTH OF NEW PRODUCT IS INDICATED BY DEVELOPMENT OF 200 (2θ) PEAK.

FIG. 28 X-RAY DIFFRACTION PATTERNS OF BENTONITE-LIME SYSTEM WITH 25% LIME ON AGING TO DIFFERENT TIME PERIOD. BROADENING OF THE PEAK AT 35° (2θ) IS SHOWN.

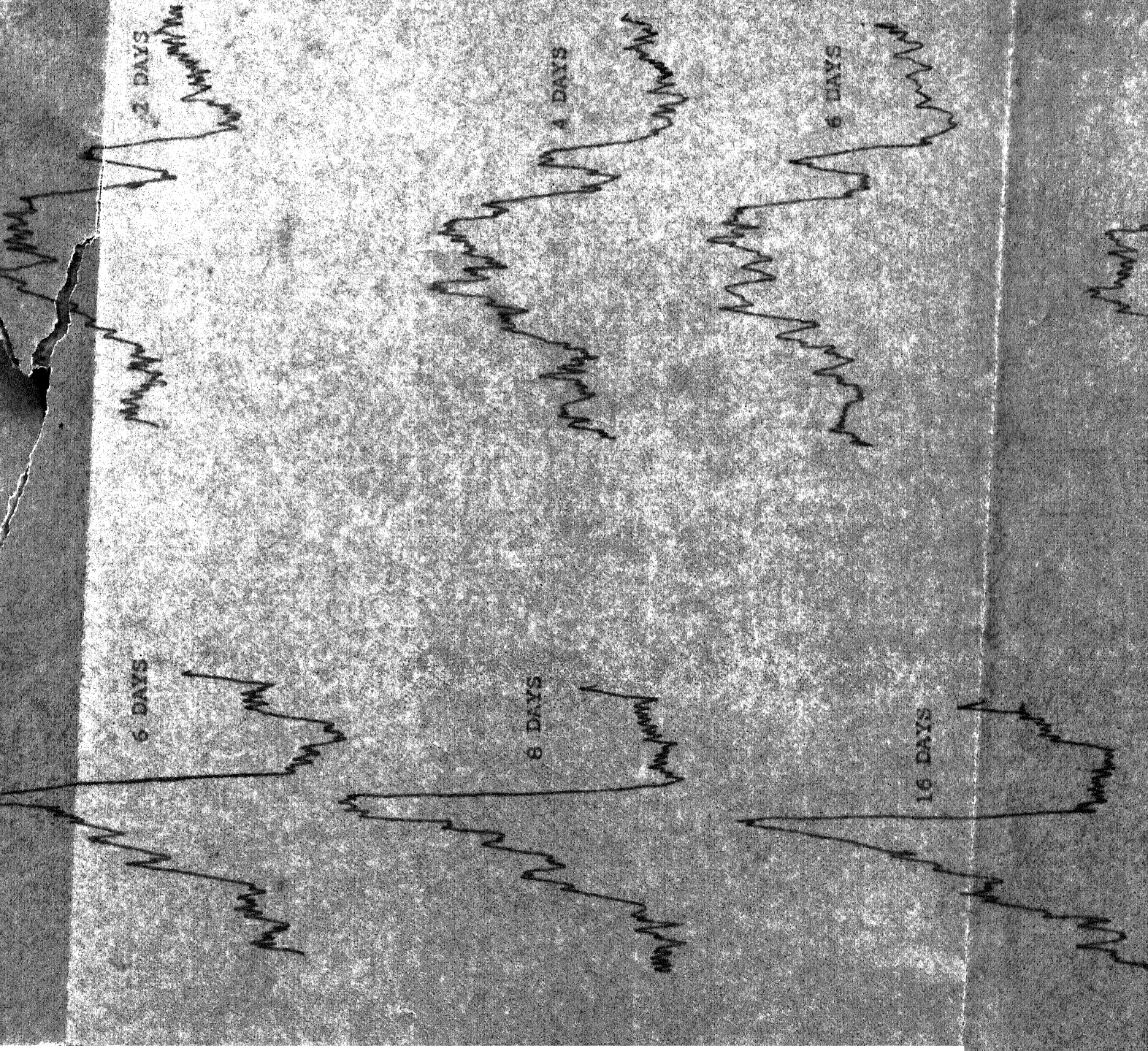


FIG. 27 X-RAY DIFFRACTION

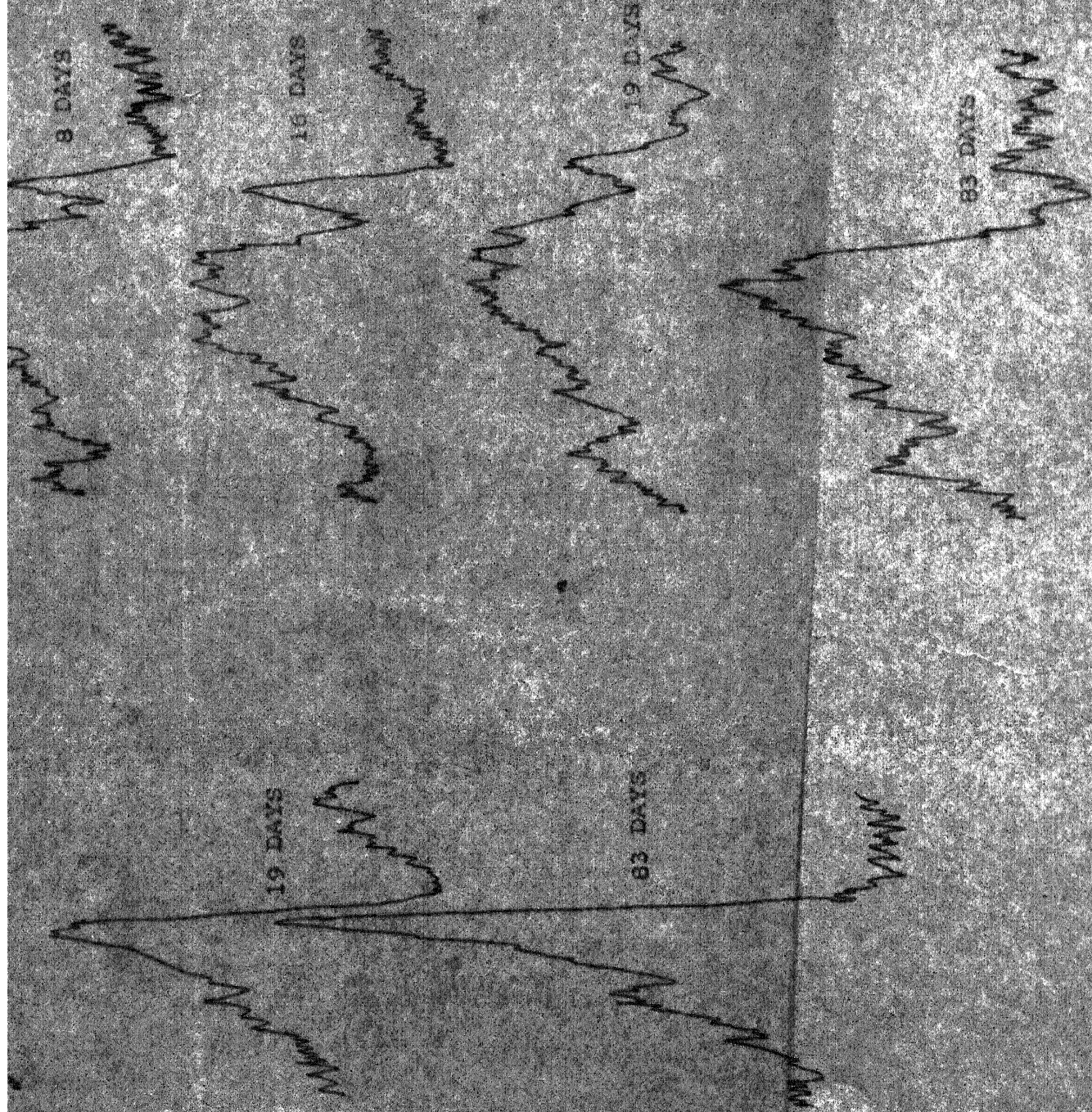


FIG. 28 X-RAY DIFFRACTION PATTERNS OF

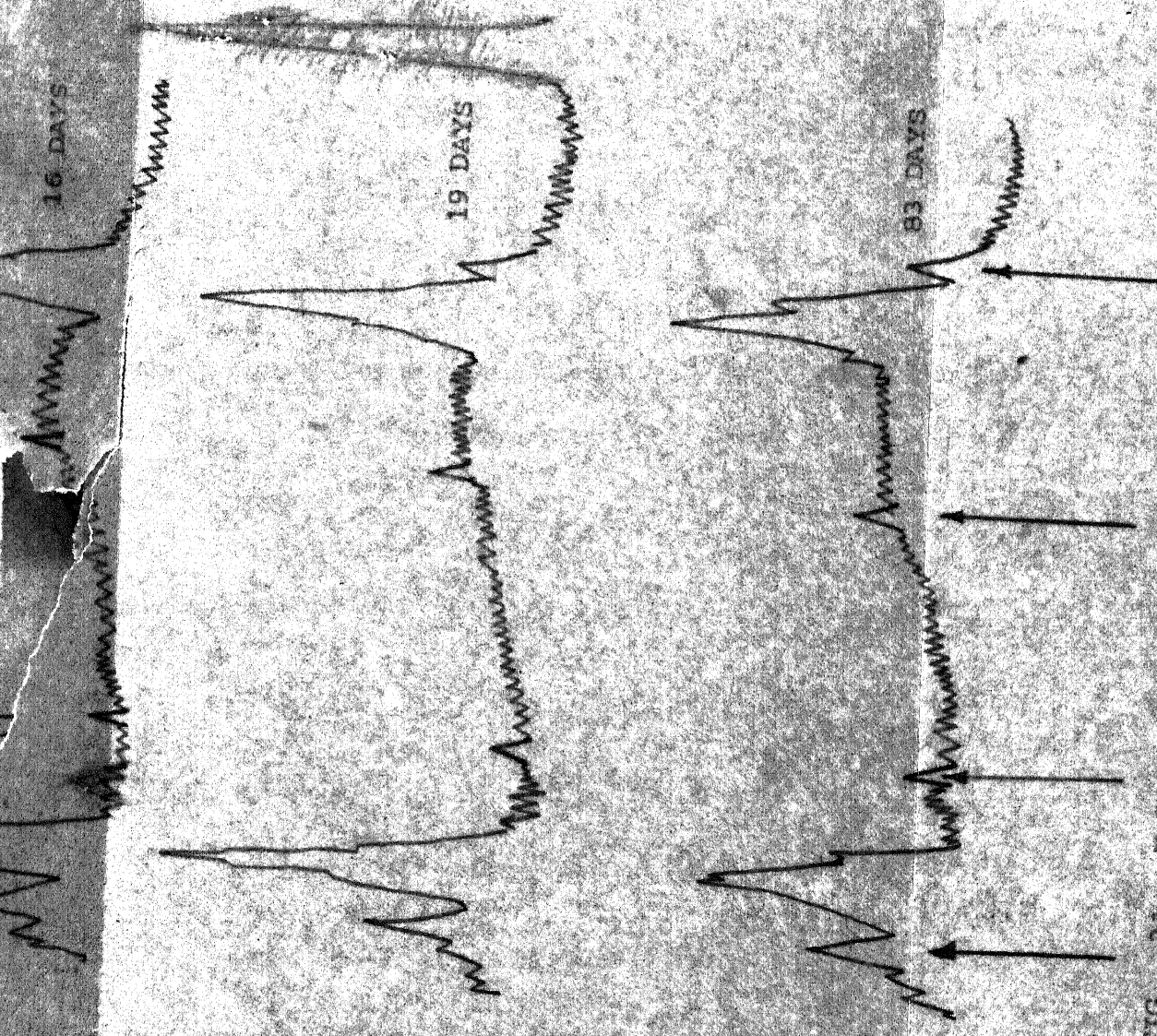


FIG. 31 X-RAY DIFFRACTION TRACES FOR KAOLINITE-LIME SAMPLE WITH 1% LIME. ARROW INDICATES NEW PRODUCTS (TETRA-CALCIUM ALUMINATE HYDRATE, CALCIUM ALUMINATE SILICATE, HYDROGARNET AND PRELIMINATE) DEVELOPED.

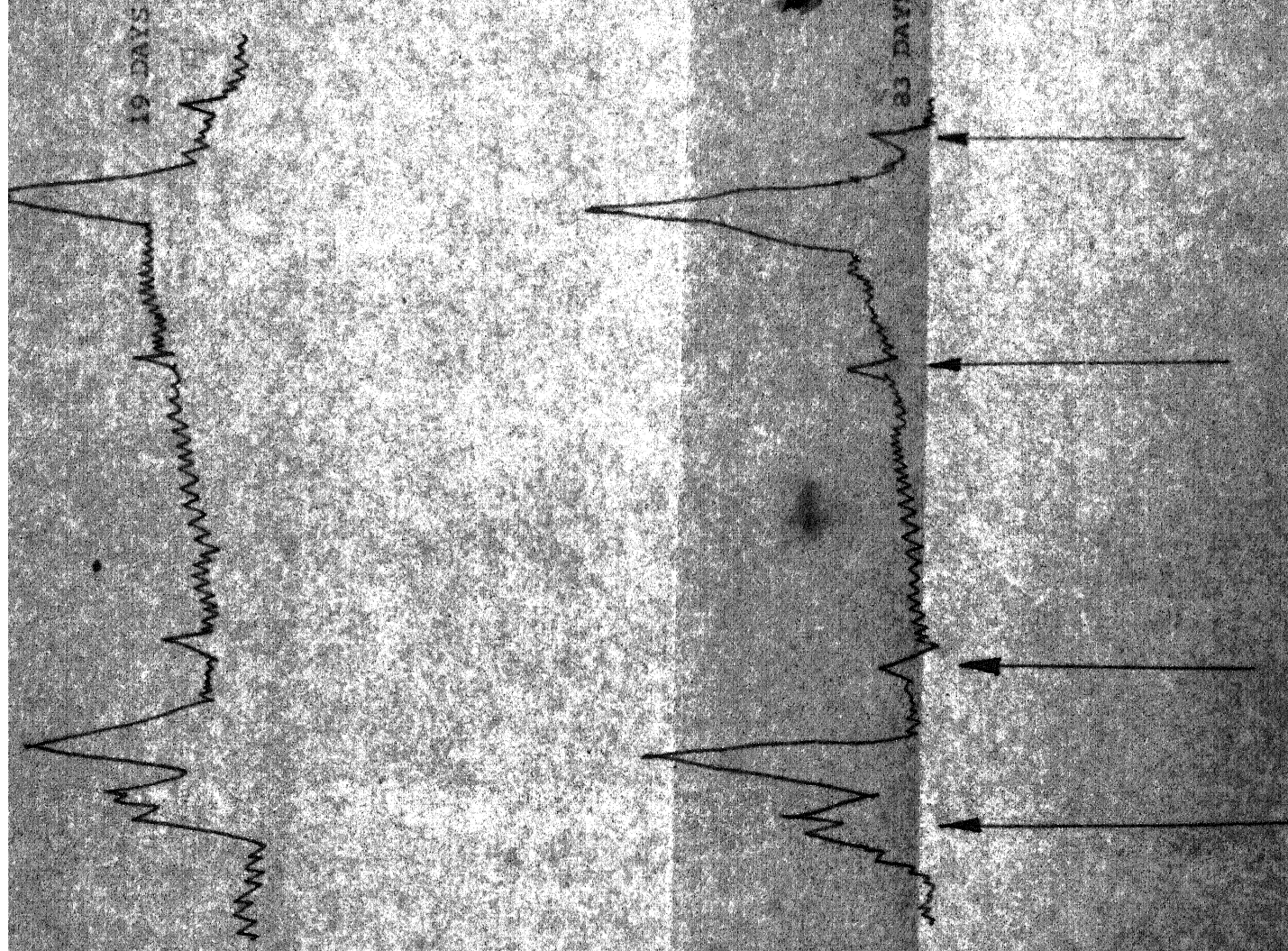
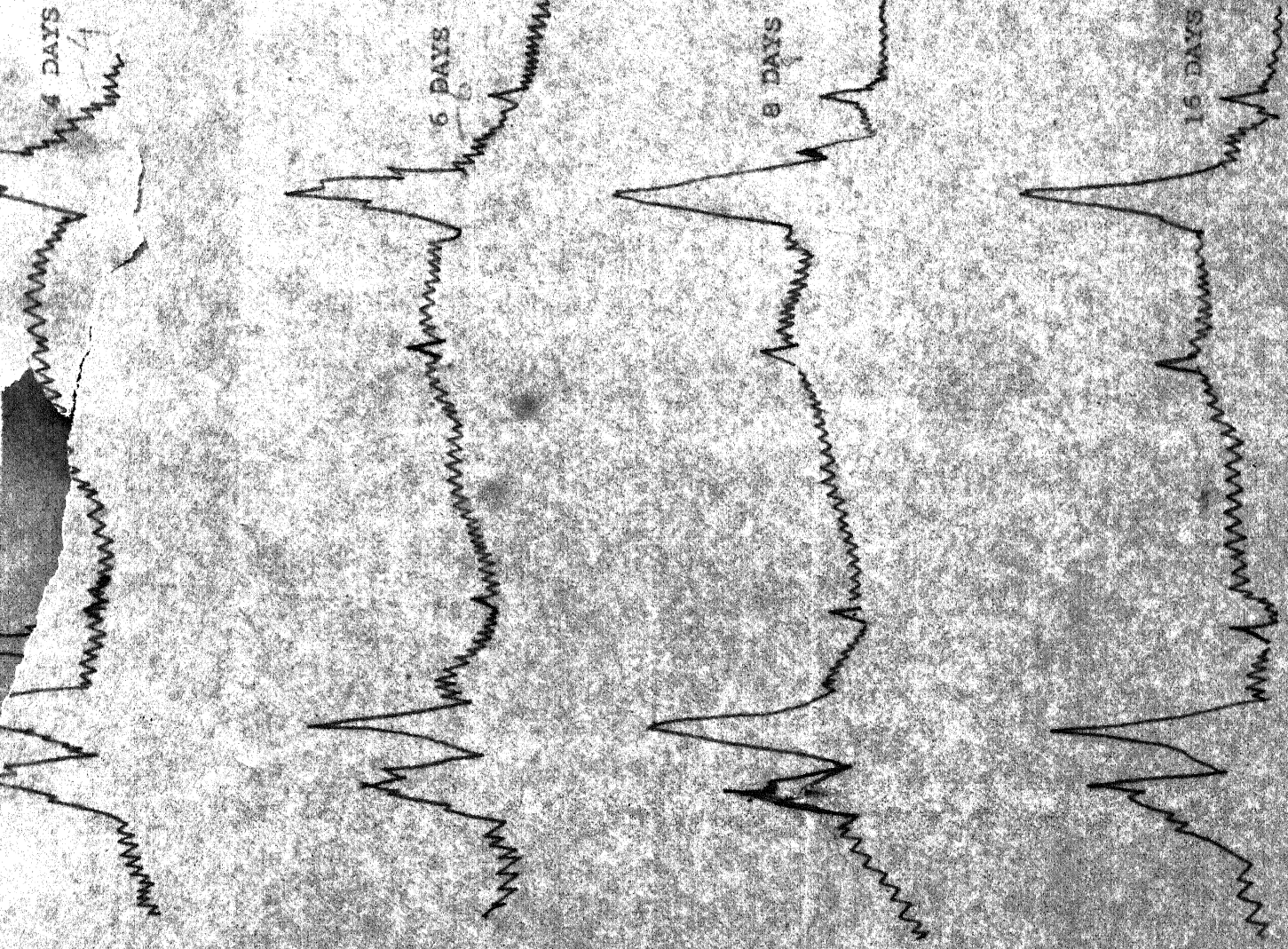


FIG. 33 X-RAY DIFFRACTION TRACES FOR MAGNETITE-LIME SAMPLE WITH 10% LIME. ARROW INDICATES NEW PRODUCTS (TETRA-CALCIUM ALUMINATE, TRIS-CALCIUM ALUMINATE, TRIS-CALCIUM ALUMINATE, TRIS-CALCIUM ALUMINATE).

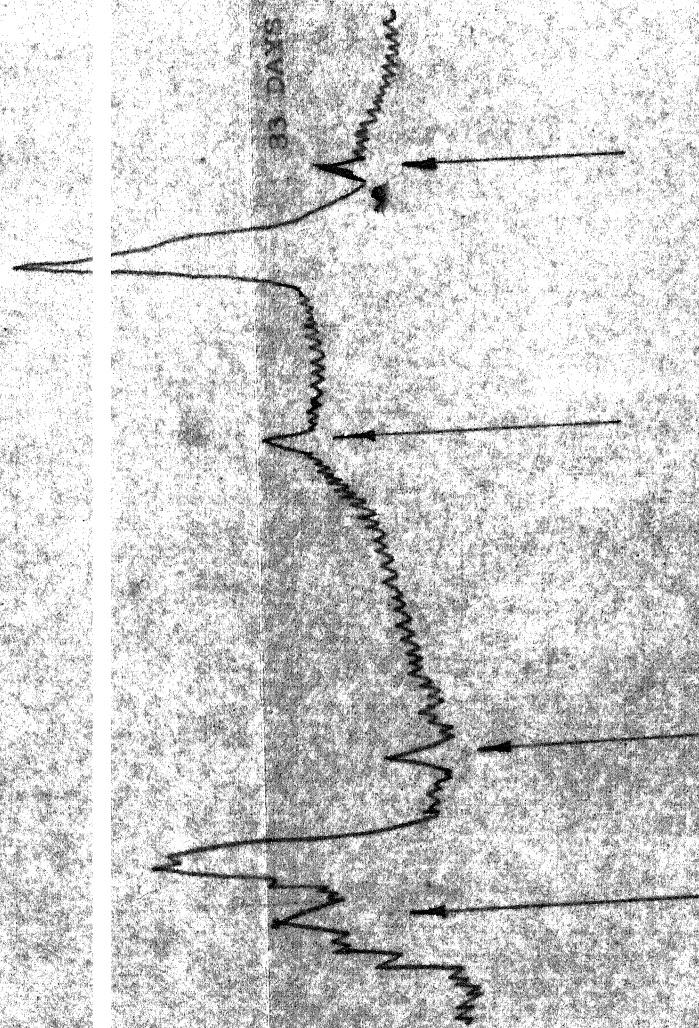


FIG. 32 X-RAY DIFFRACTION TRACES FOR KAOOLINITE -LIME
SAMPLE WITH 4% LIME. ARROW INDICATES NEW
PRODUCTS (TETRA CALCIUM ALUMINATE HYDRATE,
CALCIUM ALUMINATE SILICATE, HYDROCORNEET AND
KAOOLINITE) DEVELOPED.

CHAPTER VI

SYNTHESIS

The processes involved in the clay - lime stabilization are dependent on the nature of clay, quantity of lime available, the amount of water of hydration that is present in the system, the significant cation available for exchange by Ca-ions of the lime and the environmental conditions in case of natural soils. These changes in clay - lime system at any stage are reflected in the physical behaviour of the clay. While the Atterberg limits for any clay - lime system depend on the hydration and dehydration mechanism of the system, the strength properties are a consequence of the nature and extent of the different constituents present in the system at any stage.

Kaolinite and bentonite chosen for the study have free silica as an impurity present in the samples. The dominant clay mineral of bentonite, montmorillonite, is structurally different from kaolinite. As explained earlier the activity in bentonite as a result of lattice substitutions is responsible for adsorption, to a great extent of, exchangeable cations into its lattice. In kaolinite however such adsorption is extremely limited.

In bentonite - lime system, the adsorption of Ca-ions was upto 4 percent of lime addition into the system. The increase in calcium concentration due to the

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substitution of divalent Ca-ions for monovalent exchangeable cations in bentonite decreases repulsion and consequently ^{the} liquid limit. In kaolinite such adsorption is limited as seen from the present studies. The increase of liquid limit that is observed in the present studies has been correlated to initial saturation of Ca-ions in kaolinite (Clare and Crouchley, 1957). While this may be true, the present study indicated the possibility of prehnite (a calcium aluminate silicate), which instantaneously develops and rapidly grows in the kaolinite - lime system, influencing the liquid limit of kaolinite - lime system. The plastic limit, which is the lowest moisture content at which the bonds between the soil particles or aggregates can be constantly renewed, increases with increasing lime content in both the systems. When lime is added, Ca-ions cause a change in the electrical charge density and effect flocculation in the system. Actually with the addition of lime, more water must be added to the clay - lime system to renew the broken bonds. The significant changes of liquid and plastic limit upto 2 percent and 4 percent lime content in kaolinite and bentonite respectively point to the active role of Ca-ions during adsorption on the hydration of the clay - lime systems. Shrinkage limit in both the systems

was with an increasing trend on addition of lime. The changes in shrinkage limit were in line with the changes in the other two limits indicating the role of adsorption of Ca-ions into and onto the clay surface.

The X-ray data in the present study has revealed certain significant changes during the clay - lime interaction. Such studies have been attempted by Eades and Grim (1960) for long-term stabilization but no effort is made so far to visualize the changes that take place during the shorter periods. It was found that in both the clay minerals, kaolinite and montmorillonite, chemical reactions start simultaneously besides adsorption. In kaolinite - lime system an immediate formation of prehnite that grows with the aging as also the formation of hydrogarnets and tetra calcium aluminate hydrates has taken place, while in bentonite the formation of calcium aluminate silicates in the initial stages followed by calcium silicate hydrates, tetra calcium aluminate hydrates and *u* - crystallized tobermorites subsequently.

Detailed rate curves for the depletion of silica, kaolinite and bentonite as also the growth of new mineral prehnite in kaolinite - lime system (figures 13, 14, 16, 17 and 18) have been prepared and the role of these constituents at any stage in the clay - lime system discussed earlier. The changes in

the unconfined compressive strength in clay - lime system appears to be influenced by these new products. The increase in strength upto 4 percent can be attributed to the formation of calcium aluminate silicate. Further change in strength from 4 percent of lime to 6 percent of lime is possibly due to the additional products (Calcium silicate hydrate, tetra calcium aluminate hydrate and ill - crystallized tobermorite) formed during bentonite - lime interaction. Beyond 6 percent the strength falls down which can be very easily explained. As can be seen from the figures 13 and 14, the depletion of free silica and montmorillonite attains a stability indicating near completion of the short - term reactions. This is also confirmed by the growth of new minerals observed in X-ray patterns. As such by about 6 percent the reactions in the bentonite - lime system might have almost reached this stable phase beyond which the presence of excess of lime in the system dilutes the strength property. But in kaolinite the strength variations are somewhat strikingly different. While the initial rapid increment in strength upto 2 percent of addition of lime in kaolinite - lime system can be attributed to the rapid formation of prehnite besides Ca-ions adsorption, the subsequent fluctuations in strength upto 10 percent of lime in the system might possibly

be due to the formation of calcium silicate hydrate in gel form besides prehnite. However with increased aging due to the crystallization of calcium silicate hydrate the strength property gets modified in this range. Beyond 10 percent the crystallized minerals act as cementitious product and are responsible for the increase in strength.

Thus the observed changes in liquid, plastic, shrinkage limits and the strength parameter in the kaolinite - lime and bentonite - lime systems can be explained due to the chemical changes in these systems.

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